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Part I

SYNTHESIS AND EVALUATION OF NEW AND IMPROVED GYRO FLOTATION FLUIDS

J. S. Skelcey
The Dow Chemical Company

TECHNICAL REPORT AFML-TR-67-184, Pt I
July 1967

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SYNTHESIS AND EVALUATION OF NEW
AND IMPROVED GYRO FLOTATION FLUIDS

J. S. Skelcey

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FOREWORD

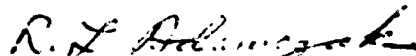
This report was prepared by The Dow Chemical Company, Midland, Michigan, on Air Force Contract Nr. AF 33(615)-5169, "Synthesis and Evaluation of New and Improved Gyro Flotation Fluids." This contract was initiated under Project Nr. 7340, "Nonmetallic and Composite Materials," and Task Nr. 734008, "Energy Transfer Fluids." The work was sponsored and administered by the Air Force Materials Laboratory, Directorate of Laboratories, Air Force Systems Command, United States Air Force, Wright-Patterson Air Force Base, Ohio, with Captain K. A. Davis as project engineer.

This report describes the work performed on the cited contract for the period 1 June 1966 to 31 May 1967. This document is Dow Report Nr. GF-4Q-67. This report was submitted by the author in July 1967.

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Management direction at Dow is under Dr. R. P. Ruh, Laboratory Director of the Scientific Projects Laboratory, and supervised by Dr. D. A. Rausch, Assistant Laboratory Director. Dr. J. S. Skelcey is the principal investigator, assisted by Mr J. E. Rumming.

This technical report has been reviewed and is approved.



R. L. ADAMCZAK, Chief
Fluid and Lubricant Materials Branch
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ABSTRACT

The objective of this research program is to produce liquids which have densities between 2.5 and 3.0 g./cc. for use as gyro flotation fluids. The work involved the synthesis of semi-inorganic compounds containing a heavy metal ion in combination with fluorocarbon anionic groups, i.e., fluorinated alkoxy, orthophosphate diesters, or β -diketones.

Hafnium and tantalum derivatives of $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$, $\text{HOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$, and $\text{HOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$ are viscous liquids with densities around 2.0 g./cc. Thallium dodecafluoroheptoxide, a low melting solid, has a density of 2.598 g./cc., whereas the density of unpurified thallium hexadecafluorononoxide is 2.48 g./cc. The thorium and lead fluoroalkoxides are solids as are all of the heavy metal derivatives of the shorter chain fluoroalcohols.

Three hydrogen orthophosphate diesters were prepared: $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$, $[(\text{CF}_3)_2\text{CHO}]_2\text{P}(\text{O})\text{OH}$ and $(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$. Heavy metal derivatives of these phosphates are all high melting solids. The four following fluorinated β -diketones were also

prepared: $\text{CF}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$, $\text{CF}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$, $\text{CH}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$ and

$\text{CH}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$. The thorium derivative of $\text{CF}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$, $\text{Th}(\text{C}_7\text{HO}_2\text{F}_{10})_4$, is a liquid whose density is 1.90 g./cc. Thallium complexes of all four of the above diketones are solids with relatively high melting points.

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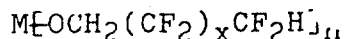
I. INTRODUCTION

The purpose of this research program is to develop liquids as candidate materials for gyro-flotation fluids. These fluids should have densities between 2.5 and 3.0 g./cc. at 125°F., viscosities between 1,000 and 5,000 cps., thermal stability at 285°F., compatibility with the various materials used in gyro construction, and good resistance to gamma radiation.

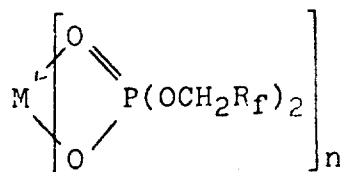
Specifically, the work involves the synthesis and characterization of semi-inorganic fluids containing a heavy metal ion from the sixth or seventh periods of the periodic table, e.g., thorium, hafnium, tantalum, cerium, mercury, thallium, lead, bismuth, etc., with a fluorinated anionic group or with a combination of anionic groups, i.e., fluorinated alkoxides, orthophosphate diesters, or β -diketonates.

The general structures of these three types of proposed heavy metal semi-inorganic compounds are:

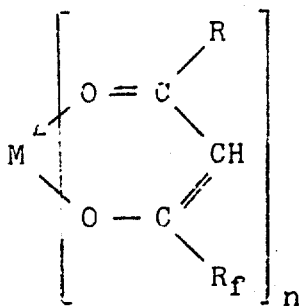
- (i) Fluoroalkoxide,



- (ii) Orthophosphate diester,



- (iii) β -Diketonate,



Presently, the most widely used gyro-flotation fluid is a polymer of $CF_2=CFBr$. This material does not have the desired chemical inertness, density or metal compatibility, and, because it is polymeric, tends to undergo thermal diffusion and stratification. To alleviate these problems encountered with polymeric materials, fluids of single molecular composition, not polymeric in structure, are preferred.

Several types of compounds were considered as potential high density liquids. The most obvious class was the highly brominated aliphatic and aromatic compounds. These materials, however, were not expected to meet the stated radiation, corrosion, and thermal stability requirements of the ideal gyro fluid.

The radiation chemistry of the organic halides has probably been studied in greater detail than that of any other type of organic compound. From these studies it has been found that, except for the C-F bond, the carbon-halogen (C-X) bond is ruptured preferentially in organic halides. The C-I, C-Br and C-Cl bonds cleave readily, whereas the C-F bond is more stable than the C-C or C-H bond (1). These results on the radiation decomposition of alkyl halides are also in accord with known bond energies (2): C-F, 116 kcal./mole; C-C, 82.5 kcal./mole; C-Cl, 81 kcal./mole; C-Br, 68 kcal./mole; and C-I, 51 kcal./mole.

A most important consequence of the radiolysis of the alkyl halides is the nature of the reaction products. Organic bromides can yield either free bromine, hydrobromic acid, or both; hydrobromic acid is the primary product. Alkyl fluorides, on the other hand, appear to degrade by C-C bond scission and do not produce a highly corrosive acid (3).

In the past, halogen-containing aromatic and aliphatic liquids have been investigated as high density fluids for applications other than gyro-flotatic fluids. In general, these fluids do not have the density and inertness required for a gyro fluid.

The alkyl bromides have been found to be highly corrosive with aluminum metal. In several cases, the bromides have been known to react explosively with aluminum through an apparent autocatalytic mechanism. Chlorocarbons were also considered for the proposed application; however, they offer no great advantage in density over the fluorocarbons and are also capable of reacting violently with aluminum.

Thus, from these considerations, it was believed that halogen compounds, other than fluorine, would not meet the required radiation and corrosion requirements.

Although the organic fluorine compounds have the desired inertness, the density of these materials reaches a maximum of approximately 2.0 g./cc. In contrast, many heavy metal compounds have densities much greater than 3.0 g./cc. These compounds, however, are generally highly ionic and consequently form solids. In order to take advantage of the density of the heavy metal compounds, an anion must be selected which will prevent crystallization from occurring and which has a sufficiently high density to prevent an appreciable lowering of the net density of the resulting fluid.

Since fluorine-containing anions have a high density and a low net interaction and lattice energy, the combination of this type of anion with heavy metal ions was expected to result in fluids meeting the target objectives.

From the known properties of metal alkoxides, phosphate diesters and β -diketonates, it was expected that the proposed compounds would meet the thermal stability requirements; however, the viscosities and corrosive properties would have to await actual testing.

II. DISCUSSION OF RESULTS

The goal of this research program was to produce liquid materials which have densities of greater than 2.5 g./cc. Work was concentrated on three types of heavy metal compounds. They are; fluoroalkoxides, phosphate diesters, and β -diketonates. The alkoxides were prepared from fluorinated alcohols which are commercially available. However, the efforts in the areas of phosphate diesters and β -diketonates included the synthesis of hydrogen phosphate diesters and β -diketones which were used as starting materials for the preparation of their metal derivatives.

A. HEAVY METAL FLUOROALKOXIDES

The program of research initially specified that the fluoroalkoxides include compounds of the following metals: thorium, tantalum, hafnium, cerium, mercury, thallium and lead. The fluoroalkoxy groups are those that are derived from dodecafluoro-1-heptanol, $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$, hexadecafluoro-1-nonol, $\text{HOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$, and dodecafluoro-2-methyl-2-octanol, $\text{HOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$. Subsequent work involved the preparation of some metal compounds with smaller chain fluoroalkoxy groups. Since the literature provides established methods for the preparation of the non-fluorinated alkoxides of most of these metals, these methods were employed for the preparation of the fluorinated alkoxides.

1. Hafnium

The hafnium fluoroalkoxides were prepared by the reactions of hafnium tetrachloride, HfCl_4 , the fluoroalcohols and ammonia in benzene:



This is essentially the method of Bradley, Menrotra and Wardlaw (4) except that they used dipyridinium hafnium hexachloride, $(\text{C}_5\text{H}_5\text{N})_2\text{HfCl}_6$, as the starting hafnium compound. Table I lists the hafnium fluoroalkoxides which have been prepared and their physical properties.

These hafnium compounds are all volatile and were purified by either sublimation or distillation. Distillation of the higher chain alkoxides could not be accomplished by normal vacuum distillation nor in a Hickman molecular still because of thermal decomposition. They could be distilled in a falling film molecular still, but even in this case some decomposition was noted. The products which were obtained were brown viscous liquids. All of the hafnium fluoroalkoxides are soluble in benzene and acetone. They are susceptible to hydrolysis especially when in solution.

TABLE I
ANALYSIS AND PHYSICAL PROPERTIES OF HAFNIUM FLUOROALKOXIDES

Compound	Analysis, wt. %				Physical Properties		
	C	H	Hf	N	M.P., °C.	B.P., °C./mm. Hg	Density, g./cc.
$\text{Hf}(\text{OCH}_2\text{CF}_3)_4$	16.90	1.74	30.10	2.13	106-107	Sublimes	---
	Theory 16.70	1.39	31.10	--		95/0.005	
$\text{Hf}(\text{OCH}_2\text{C}_2\text{F}_5)_4$	18.34	1.44	22.33	2.09	96-99	Sublimes	---
	Theory 18.60	1.03	23.05	--		80/0.01	
$\text{Hf}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$	21.85	1.11	11.90	0.43	---		
	Theory 22.38	0.80	11.88	--	---	245/0.003	2.00 at 25°C.
$\text{Hf}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$	26.35	1.92	10.80	0.30	---		
	Theory 26.76	1.73	11.06	--	---	210/0.005	1.79 at 21°C.
$\text{Hf}[\text{OCH}_2(\text{CH}_2)_7\text{CF}_2\text{H}]_4$	20.75	0.73	10.20	0.30	---		
	Theory 22.70	0.64	9.38	--	---	250/<0.001	2.05 at 23°C.

In reference to Table I, it will be noted that analysis has revealed the presence of nitrogen in the hafnium fluoroalkoxides. The IR spectra show evidence of nitrogen-hydrogen bonds by the absorptions in the region near three microns. This was also verified by proton NMR data. Assuming that the nitrogen is in the form of ammonia, then the compositions of the trifluoroethoxide and pentafluoropropoxide approach those of the ammine complexes, $\text{Hf}(\text{OCH}_2\text{CF}_3)_4 \cdot \text{NH}_3$ and $\text{Hf}(\text{OCH}_2\text{C}_2\text{F}_5)_4 \cdot \text{NH}_3$. The ammine species is bonded strongly enough that it is not lost during the vacuum sublimation of these materials at temperatures near 90°C . There is also better agreement between the elemental analysis and theoretical composition if it is based upon an ammine complex. Thus, $\text{Hf}(\text{OCH}_2\text{CF}_3)_4 \cdot \text{NH}_3$ requires 16.24% C, 1.87% H, 30.17% Hf, and 2.37% N, while $\text{Hf}(\text{OCH}_2\text{C}_2\text{F}_5)_4 \cdot \text{NH}_3$ requires 18.20% C, 1.40% H, 22.54% Hf and 1.77% N. Compared to the reported data in Table I, there is close agreement. Although these data support the existence of ammine complexes of $\text{Hf}(\text{OCH}_2\text{CF}_3)_4$ and $\text{Hf}(\text{OCH}_2\text{C}_2\text{F}_5)_4$, it is known that Group IV transition metals generally do not form stable ammine complexes. D. C. Bradley and coworkers (4) have not reported any data on such complexes during their work on transition metal non-fluorinated alkoxides.

The three longer chain fluoroalkoxides of hafnium have less nitrogen associated with them (N/Hf atom ratio = 0.35-0.46) and do not approach the compositions of the trifluoroethoxide and pentafluoropropoxide. These materials, $\text{Hf}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$, $\text{Hf}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$ and $\text{Hf}[\text{OCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}]_4$, were vacuum distilled at temperatures above 210°C . and may have lost some of the ammonia during this process. The proton NMR spectra of these compounds were less definite for the N-H analysis because of the small amounts associated with them.

Although the nature of these hafnium fluoroalkoxides have not been definitely proven, work in this area was de-emphasized in order to investigate the fluoroalkoxides of the other metals. The densities were slightly lower than expected; however, it is interesting to note the increase of 0.2 g./cc. in going from the tertiary alkoxide, $\text{Hf}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$, to the primary alkoxide, $\text{Hf}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$. It is expected that more work will be done on hafnium compounds. It has been shown that liquid hafnium fluoroalkoxides can be prepared, and future work will investigate alcohols which, when combined with hafnium, will yield liquids of higher densities than presently attained.

2. Tantalum

To synthesize the fluoroalkoxides of tantalum, tantalum ethoxide, $\text{Ta}(\text{OC}_2\text{H}_5)_5$, was first prepared and then used in alcohol exchange reactions with the fluoroalcohols. The method of Bradley, Wardlaw, and Whitley (5) was used to prepare $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and is essentially

the same procedure for preparing the hafnium fluoroalkoxides. Tantalum ethoxide was purified by distillation at 126°C. and 0.11 mm. Hg and identified by its IR spectrum. Tantalum tri-fluoroethoxide was also prepared by this method and purified by vacuum sublimation at 95°C. and 0.02 mm. Hg. This material is a white solid which melts at ~95°C. By elemental analysis the product was found to be 17.34% C, 1.44% H, and 26.2% Ta. The calculated analysis for $\text{Ta}(\text{OCH}_2\text{CF}_3)_5$ is 17.25% C, 1.49% H, and 26.8% Ta.

The longer chain fluoroalkoxides of tantalum were prepared by alcohol exchange reactions of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ with an excess of the appropriate fluoroalcohol:



In general, the reactions were run in refluxing benzene or toluene, and the ethanol which was produced was removed by azeotropic distillation and collected in a Dean-Stark trap. Table II lists the tantalum fluoroalkoxides produced by this method and their physical properties.

It is immediately recognized from the compounds listed in Table II that complete substitution of the ethoxy groups by the fluoroalkoxy groups was not accomplished by the exchange reactions. The most complete substitution occurred at a higher temperature when toluene was used as the solvent. These results, in the case of dodecafluoroheptanol reactions, are in contrast to those reported by W. Wardlaw (6) for the non-fluorinated alkoxides of tantalum. He reported that alcohol interchange reactions readily occur with $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and other primary alcohols; however, secondary and tertiary alcohols replace only four of the groups. In the case of the tertiary alcohol, $\text{HOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$, only three ethoxy groups were replaced after nine hours in refluxing benzene.

The properties of the fluorinated alkoxides of tantalum are similar to those of the hafnium compounds which were already mentioned. Like the hafnium compounds, the densities of these materials appear to approach a maximum near 2.0 g./cc., and, therefore, they are of no immediate interest. Since $\text{Ta}(\text{OCH}_2\text{CF}_3)_5$ was easily prepared by the reaction of tantalum pentachloride, trifluoroethanol and ammonia in benzene it is likely that the higher chain fluoroalkoxides could also be prepared by this type of reaction. The problem of the formation of the amine type compounds was not investigated for $\text{Ta}(\text{OCH}_2\text{CF}_3)_5$ and it is not known if this would occur as it does with the hafnium fluoroalkoxides.

TABLE II
ANALYSIS AND PHYSICAL PROPERTIES OF TANTALUM FLUOROALKOXIDES

Compound	Analysis, wt. %			Physical Properties	
	C	H	Ta	B.P., °C./ mm. Hg	Density, g./cc.
$\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4[\text{OC}_2\text{H}_5]$	23.15	1.27	12.80	250/<0.001	---
Theory	23.12	1.10	11.69		
$\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_{4.3}[\text{OC}_2\text{H}_5]_{0.7}$ ^{a, b}				260/0.001	2.01 at 24°C.
$\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_{4.7}[\text{OC}_2\text{H}_5]_{0.3}$ ^a				255/<0.001	2.02 at 23°C.
$\text{Ta}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_3[\text{OC}_2\text{H}_5]_2$	27.45	2.48	13.3	250/0.005	---
Theory	27.60	2.30	13.4		

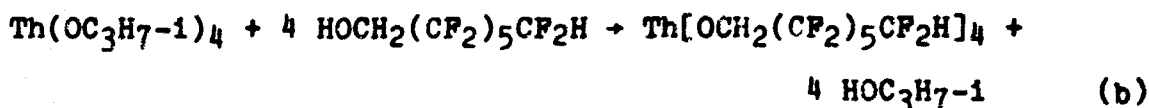
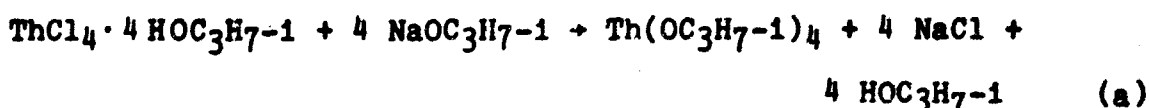
^aComposition determined by proton NMR.

^bStarting tantalum compound was $\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4[\text{OC}_2\text{H}_5]$.

3. Thorium

The reactions which were run in attempts to prepare the thorium fluoroalkoxides have not provided as positive results as those obtained for the hafnium and tantalum compounds. Nevertheless, sufficient data were obtained in addition to that already published for the non-fluorinated alkoxides of thorium to reasonably predict that extensive efforts in this area would not be justified.

An attempt was made to synthesize thorium dodecafluoroheptoxide, $\text{Th}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$, by the following reactions:

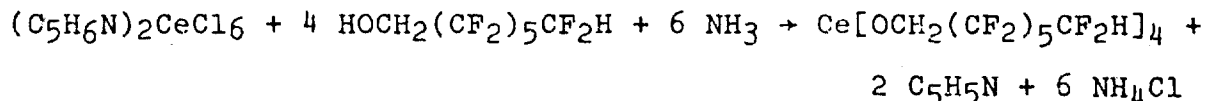


This is the method of Bradley, Saad, and Wardlaw (7) for preparing thorium alkoxides. Reaction (a) was run in isopropanol and it was assumed that the soluble white solid from this reaction was $\text{Th}(\text{OC}_3\text{H}_7-1)_4$. Reaction (b) was run in benzene and the product obtained from it contained 4.3% sodium and only 0.3% thorium which indicates that very little $\text{Th}(\text{OC}_3\text{H}_7-1)_4$ was produced in Reaction (a). The preparation of thorium hexadecafluorononoxide, $\text{Th}[\text{OCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}]_4$, was accomplished by the reaction of $\text{NaOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$ and $\text{ThCl}_4 \cdot 4 \text{HOC}_3\text{H}_7-1$ in diethyl ether. The sodium salts of the fluoroalcohols can be made by the reaction of the alcohols with sodium metal in diethyl ether; however, the reaction of the alcohols with sodium hydride is much faster and cleaner. After the $\text{ThCl}_4 \cdot 4 \text{HOC}_3\text{H}_7-1$ was added and the mixture stirred for 24 hours at room temperature, the soluble product was recrystallized from benzene. The less soluble was mainly $\text{Th}[\text{OCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}]_4$ which deposited out as white crystals. It had the following composition: 20.75% C, 0.67% H, 11.6% Th, 0.03% Cl and 3.0% Na, whereas $\text{Th}[\text{OCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}]_4$ requires 22.1% C, 0.61% H, and 11.85% Th. The more soluble fraction was chiefly $\text{NaOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$. It was not unexpected that this thorium fluoroalkoxide is a solid since the non-fluorinated alkoxides of thorium are known to have more ionic character than the other Group IV metal alkoxides and, thus, should have less volatility. This is exemplified by the fact that the primary and secondary alkoxides of thorium are solids (7,8,9); however, the tertiary alkoxides of thorium are distillable liquids (10). A few attempts were made to prepare thorium dodecafluoro-2-methyl-2-octoxide, $\text{Th}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4$, to ascertain if this fluorinated tertiary alkoxide would also be a liquid. However, in each case no thorium fluoroalkoxide could be isolated. The first reaction tried was that of $\text{ThCl}_4 \cdot 4 \text{HOC}_3\text{H}_7-1$ and $\text{NaOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$.

in diethyl ether. The second was that of dipyridinium thorium hexachloride, $(C_5H_5N)_2ThCl_6$, and $NaOC(CH_3)_2(CF_2)_5CF_2H$ in benzene. Since these reactants are slightly ionic, it was decided that a more polar solvent was needed and, therefore, the reaction was repeated using tetramethylenesulfone, $(CH_2)_4SO_2$, as the medium. The results indicate that not enough care was taken to keep moisture out of the reaction, since the products were those expected from hydrolysis. Further efforts on this phase of the research were discontinued because it did not seem likely that the density of $Th[OC(CH_3)_2(CF_2H)]_4$ would reach 2.5 g./cc. even if it was a liquid.

4. Cerium

Work on the synthesis of cerium fluoroalkoxides involved the reaction of dipyridinium cerium hexachloride, $(C_5H_5N)_2CeCl_6$, $HOCH_2(CF_2)_5CF_2H$ and ammonia in benzene. The $(C_5H_5N)_2CeCl_6$ was prepared by the method of Bradley, Chatterjee and Wardlaw (8). A suspension of this material in benzene was treated with excess alcohol and ammonia according to the following equation:



A soluble, brown, glassy substance was isolated from the reaction and could not be freed of unreacted alcohol by vacuum pumping. Recrystallization attempts in benzene, a benzene-hexane mixture, and acetone were unsuccessful. The product was extremely sensitive to atmospheric moisture. A second attempt was made to prepare $Ce[OCH_2(CF_2)_5CF_2H]_4$ by the above reaction; however, essentially the same results were obtained. Results of an elemental analysis of the product did not approach that calculated for $Ce[OCH_2(CF_2)_5CF_2H]_4$. There is a similarity between cerium and thorium since they both form ionic type alkoxides, and thus, cerium fluoroalkoxides are expected to be solids. Therefore, the efforts to prepare them were not continued.

5. Thallium

Research on compounds of metals with oxidation states of +4 and +5 indicated that the target density would not be reached with them. The ratio of organic groups to metal is obviously too high and, in effect, the weight of the metal is diluted by the less dense organic material. Therefore, the emphasis of the research on metal fluoroalkoxides was shifted to those metals of lower valency. Of greatest interest were the compounds of thallium(I) because many of the non-fluorinated alkoxides of this

metal are known to be dense liquids. Thallium ethoxide, TlOC_2H_5 , is a yellowish oil with a density of 3.52 g./cc. at 20°C . (11). However, like most thallium alkoxides, TlOC_2H_5 is not very thermally stable and is decomposed at temperatures above 130°C .

In general, the thallium fluoroalkoxides can be prepared by the reaction of thallium hydroxide, TlOH , and an excess of the fluoroalcohol at room temperature. The following equation represents the reaction:



This is an apparent equilibrium reaction since not all of the hydroxide reacts. Reaction times have usually been longer than 24 hours, although there are no data as to when equilibrium is reached. The products are isolated by filtering off the unreacted hydroxide and removing the excess alcohol by vacuum evaporation. Table III lists the thallium fluoroalkoxides which have been prepared by this method and their physical properties.

In general, a of the thallium fluoroalkoxides are white or light yellow solids. They have been observed to dissolve in acetone, diethyl ether and the fluoroalcohols from which they were made. Acetone solutions of these compounds are susceptible to hydrolysis. The volatilities of all of the materials were not determined. Thallium trifluoroethoxide can be vacuum sublimed, but the melting range of the sublimate was $93^\circ\text{--}120^\circ\text{C}$. Thallium dodecafluoroheptoxide cannot completely be freed of the unreacted alcohol unless it is distilled in a falling film molecular still. Even though the IR spectrum of the undistilled product may show very little O-H absorption around 3 microns, elemental analysis indicates up to 0.45 mole of alcohol per mole of alkoxide. Freshly distilled $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ is a clear light yellow liquid which slowly crystallizes to a greasy solid upon standing for approximately one week at room temperature. The melting point of a completely solidified sample was observed to be over the range of $40^\circ\text{--}54^\circ\text{C}$. The density of freshly distilled $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ is 2.598 g./cc. at 25°C . and exceeds the target density of 2.5 g./cc. At the present time the compound is the best candidate for a gyro-flotation fluid; however, its relatively high melting point may be a drawback.

Compared to $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$, it would be predicted that $\text{TlOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$ would be a liquid or, at least, have a lower melting point. Since the two methyl groups on the α -carbon are electron releasing groups, the metal-oxygen bond in $\text{TlOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$ should exhibit more covalent character than that of $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$. This trend, increased volatility of

TABLE III
ANALYSIS AND PHYSICAL PROPERTIES OF THALLIUM FLUOROALKOXIDES

Compound	Analysis, Wt. %				Physical Properties		
	C	H	Tl ^a	M.P., °C.	B.P., °C. Sublimes 40/0.02 mm. Hg.	Density, g./cc.	
TlOCH ₂ CP ₃	8.53	0.78	62.39	97-100	---	---	
Theory	7.91	0.66	67.37	~50	---	---	
TlOCH ₂ C ₂ F ₅	10.29 10.19	0.59 0.57	56.64 57.83		---	---	
Theory							
TlOCH(CF ₃) ₂	9.70 9.70	0.30 0.27	55.01 55.03	85-88	---	---	
Theory							
TlOCH ₂ C ₃ F ₇	11.95 11.91	0.60 0.50	50.66 50.66	73	---	---	
Theory							
TlOCH ₂ (CF ₂) ₃ CP ₂ H	14.00 13.79	0.78 0.69	45.60 46.93	83	---	---	
Theory							
TlOCH ₂ (CF ₂) ₅ CP ₂ H	15.90 15.70	0.64 0.56	38.04 38.17	40-54	200/<0.001 mm. Hg	2.598 at 25°C.	
Theory							
TlOC(CH ₃) ₂ (C ²) ₅ CP ₂ H	19.25 19.18	1.38 1.25	34.60 36.27	74-76	---	---	
Theory							
TlOCH ₂ (CF ₂) ₇ CP ₂ H ^b	16.45 17.01	0.30 0.48	31.91 32.16	---	---	2.48 at 23°C.	
Theory							

^a Corrected.^b Reaction run at 75°C.

primary alkoxides compared to tertiary alkoxides, was previously noted in the discussion on thorium compounds. However, in the case of thallium the tertiary fluoroalkoxide, $\text{TlOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$, melts approximately 20 degrees above the corresponding primary alkoxide, $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$.

Thallium hexadecafluorononoxide was prepared from the alcohol and hydroxide at 75°C . in order to liquefy the alcohol which melts at 66°C . After filtration, the excess alcohol was removed by vacuum sublimation to yield liquid $\text{TlOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$ which has a density of 2.48 g./cc. This material was not distilled and the elemental analysis shows low values for carbon and hydrogen. It is probable that when a purified sample of this compound is obtained its density will exceed 2.5 g./cc. It is also possible that upon purification it will crystallize like $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$.

The work on the thallium fluoroalkoxides is being continued. A large sample (~150 g.) of $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ has been prepared and distilled. As soon as analytical data are received on this material, its viscosity, toxicity, thermal stability, and corrosiveness will be determined. Secondly, a method for the purification of $\text{TlOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$ will be worked out in order that accurate density and melting point measurements can be made.

6. Lead

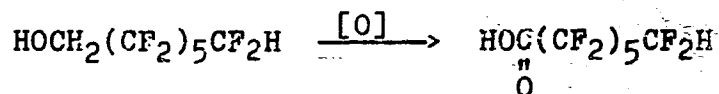
Since the fluoroalkoxides of the lower valency metals offered the best hope of obtaining high density liquids, work was undertaken on the preparation of lead(II) fluoroalkoxides. The nonfluorinated lead(II) alkoxides are not well known; however, there have been reports on their preparations (12, 13). Lead ethoxide diethanolate, $\text{Pb}(\text{OC}_2\text{H}_5)_2 \cdot 2\text{HOC}_2\text{H}_5$, is a crystalline solid which is sensitive to air and decomposes to lead oxide upon prolonged drying under vacuum (13). This compound was prepared in ~40% yield by the reaction of lead chloride and potassium ethoxide in ethanol. Since the fluorinated alcohols are more acidic than the nonfluorinated alcohols, it was decided to investigate the reactions of lead hydroxide, $\text{Pb}(\text{OH})_2$, with the fluorinated alcohols. The following equation represents the reaction:



This is analogous to the reaction for the preparation of thallium fluoroalkoxides.

In an attempt to prepare $\text{Pb}(\text{OCH}_2\text{CF}_2)_2$, a mixture of $\text{Pb}(\text{OH})_2$ and HOCH_2CF_2 was refluxed (74°C .) for sixteen hours; however, only the starting materials were recovered. When $\text{Pb}(\text{OH})_2$ and $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ were heated to reflux ($\sim 150^\circ\text{C}$.) under slight vacuum, apparent decomposition of the alcohol occurred on the surface of the $\text{Pb}(\text{OH})_2$. From this reaction mixture was isolated a soluble, greasy

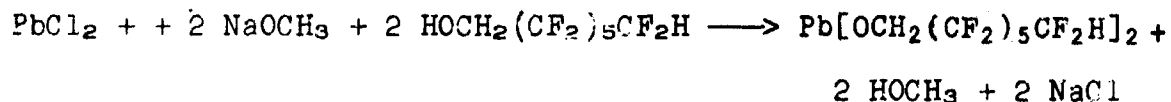
brown material having an IR spectrum which had, besides the expected absorptions, an additional absorption in the carbonyl region around 6.1 microns. The proton NMR spectrum revealed that the mole ratio of $-CF_2H$ (terminal group hydrogens) to $-CH_2-$ groups (α -carbon hydrogens) was 8:1. This product could not definitely be identified, but these data suggest partial oxidation of the alcohol to the acid:



The resulting product was most likely a mixture of the lead alkoxide and carboxylate. Oxidation may have been due to lead nitrate which was later found by X-ray diffraction analysis to be present in the $Pb(OH)_2$.

Lead hydroxide and $HOCH_2(CF_2)_5CF_2H$ were made to react in refluxing benzene with removal of the water by azeotropic distillation. The soluble, brown, viscous liquid which was isolated was heated to $90^\circ C$. in vacuo for four hours to remove the unreacted alcohol. Since the IR spectrum still showed the presence of alcohol, the product was heated an additional five hours at $120^\circ C$. in vacuo. There was apparent decomposition during this heating and this is indicated in the elemental analysis. This material was found to contain 15.93% C, 0.65% H and 31.6% Pb. The reaction was repeated; however, freshly precipitated $Pb(OH)_2$ was used instead of the commercial grade material. After refluxing for ten days, 8.8 g. of a soluble, white, waxy solid was obtained from 7.5 g. of $Pb(OH)_2$. This product was heated to $55^\circ C$. in vacuo for five days to remove the unreacted alcohol. Although the IR spectrum of this product appeared as expected for $Pb[OCH_2(CF_2)_5CF_2H]_2$, the elemental analysis indicated otherwise. It gave 16.34% C, 0.70% H, and 29.4% Pb, whereas theory requires 19.34% C, 0.70% H, and 23.83% Pb. The properties of this material may be similar to those of $Pb(OC_2H_5)_2 \cdot 2HOC_2H_5$ which yields PbO upon prolonged vacuum drying. The elemental analysis, at least, shows the presence of another lead compound besides the fluoroalkoxide. In an attempt to obtain a melting point in a sealed capillary, the material softened at $79^\circ C$., began to turn brown at $180^\circ C$., and decomposed with bubbling at $240^\circ C$. This sample of lead fluoroalkoxide could probably be purified by recrystallization; however, its high melting point and apparent instability makes it of little interest to the objectives of this project.

Another reaction which was run in an attempt to prepare $Pb[OCH_2(CF_2)_5CF_2H]_2$ is represented by the following equation:



With refluxing benzene as the solvent, the HOCH_3 was distilled from the mixture to yield a soluble, brown, viscous material which was vacuum dried. Upon standing at room temperature for approximately two weeks, this product began to crystallize. Elemental analysis gave only 0.60% Pb for this material. A plausible explanation for this is that the reaction was essentially that of NaOCH_3 and $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ to yield $\text{NaOCH}_2(\text{CF}_2)_5\text{CF}_3$, with very little reaction of the PbCl_2 .

In conclusion, only two reactions yielded products which could be considered as a lead fluoroalkoxide. They appeared to be so sensitive to heat and moisture that no attempts were made to work out a purification procedure. From appearance, the best product was obtained from the reaction of freshly precipitated $\text{Pb}(\text{OH})_2$ and $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ in refluxing benzene. It is a white solid, and, most likely, if the product from the other reaction could be purified, it would also be a solid. Thus, it is possible to prepare lead(II) fluoroalkoxides, but their chemical and physical properties do not meet the specifications for use as a gyro fluid.

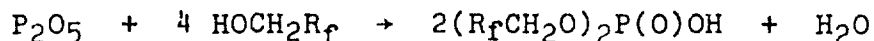
7. Mercury

A few experiments were tried in an effort to prepare mercuric dodecafluoroheptoxide, $\text{Hg}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]$; however, no definite results were obtained. Mercuric acetate, $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$, and $\text{NaOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ were made to react in methanol at room temperature. Products which were identified included HgO , $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ and unreacted $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$. There was no reaction when $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ were heated to 100°C . for two hours. Under advisement, work on these compounds was discontinued because, even if they could be prepared, most likely they would react with the materials of construction of a gyroscope.

B. HEAVY METAL PHOSPHATE DIESTERS

Three dialkyl hydrogen phosphates which were proposed were prepared, characterized, and finally used in the synthesis of the heavy metal compounds. These phosphates are: bis(pentafluoropropyl) hydrogen phosphate, $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$; bis(hexafluoroisopropyl) hydrogen phosphate, $[(\text{CF}_3)_2\text{CHO}]_2\text{P}(\text{O})\text{OH}$; and bis(heptafluorobutyl) hydrogen phosphate, $(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$. The proposed metal derivatives of these phosphates included those of thorium, tantalum, thallium, lead, mercury, and bismuth.

The initial reaction used for the preparation of the hydrogen phosphate compounds is represented by the following equation:



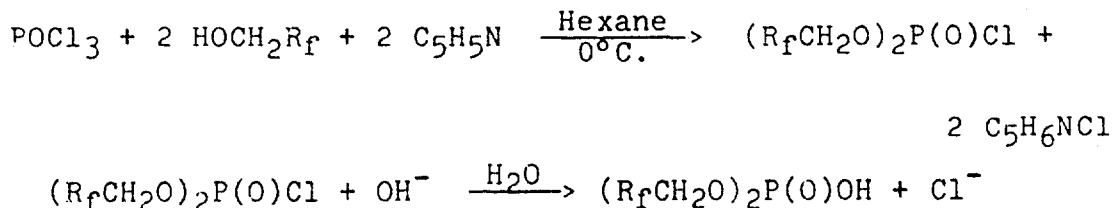
The mixture of P_2O_5 and the alcohol in hexane was maintained at room temperature until the disappearance of the P_2O_5 , at which time it was then heated to reflux for at least three hours. After vacuum stripping of the solvent and unreacted alcohol, the phosphate diester was purified by molecular distillation. Table IV lists these compounds with their boiling points and analytical data.

TABLE IV
ANALYSIS AND PROPERTIES OF BIS(FLUOROALKYL)HYDROGEN PHOSPHATES

Compound	Analysis, Wt. %				Appearance	B.P., °C./mm. Hg
	C	H	P	F		
$(C_2F_5CH_2O)_2P(O)OH$	19.55	1.41	8.65	52.3	Liquid	190/0.02
Theory	19.89	1.38	8.56	52.49		
$[(CF_3)_2CHG]_2P(O)OH$	18.10	0.87	6.83	56.25	Low melting solid	180/1
Theory	18.09	0.75	7.79	57.29		
$(C_3F_7CH_2O)_2P(O)OH$	19.13	1.21	8.89	---	Low melting solid	205/<0.001
Theory	20.78	1.08	6.71	57.58		

The yields of these reactions were fairly low (~40%), and at times the isolation and purification steps required a considerable amount of time. This was especially true when the preparations were scaled up. As an example, an attempt was made to prepare 150 g. of $(C_2F_5CH_2O)_2P(O)OH$ by the reaction of P_2O_5 and $HOCH_2C_2F_5$. After the normal reaction procedure, the elemental analysis of the distilled product proved that it consisted of 35% of the diester, $(C_2F_5CH_2O)_2P(O)OH$, and 65% of the monoester, $C_2F_5CH_2CP(O)(OH)_2$. Similarly, only the monoester, $C_3F_7CH_2OP(O)(OH)_2$, was obtained when P_2O_5 and $HOCH_2C_3F_7$ were made to react. When an attempt was made to further esterify this compound to the diester by reacting it with $C_3F_7CH_2OH$ in refluxing benzene, an azeotropic mixture of benzene and $C_3F_7CH_2OH$ distilled out at ~75°C. There was some success in separating the monoester-diester mixtures by neutralizing an aqueous solution of them with barium hydroxide and collecting the more insoluble barium salt of the diester. This can then be converted to the hydrogen phosphate diester by treatment with sulfuric acid.

Because of these problems incurred during the preparations of the diesters, a different method was investigated. This involved the reactions of phosphoryl chloride, POCl_3 , and the fluoroalcohols to obtain the chlorophosphates, $(\text{R}_f\text{CH}_2\text{O})_2\text{P}(\text{O})\text{Cl}$, which can be hydrolyzed to the acid, $(\text{R}_f\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$. These reactions are represented by the following equations:



For example, bis(pentafluoropropyl)chlorophosphate, $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{Cl}$, was obtained by the reaction of POCl_3 , $\text{HOCH}_2\text{C}_2\text{F}_5$ and pyridine in hexane, and distilled at 40°C . and 0.3 mm. Hg. Elemental analysis gave 18.45% C, 1.09% H, 8.01% P, and 11.10% Cl, whereas theory for $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{Cl}$ is 18.75% C, 1.05% H and 9.23% Cl. This chlorophosphate was then hydrolyzed in aqueous caustic to produce the acid, $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$, which was distilled at 190°C . and 0.02 mm. Hg. Subsequent studies have shown that the chlorophosphates need not be isolated, but can be hydrolyzed in the original reaction mixture to produce the acid.

Various methods were investigated in the synthesis of the heavy metal derivatives of the phosphate diesters. However, the work at this time has not yielded products which are liquids.

Thallium bis(hexafluoroisopropyl)phosphate, $\text{TlOP}[\text{OCH}(\text{CF}_3)_2]_2$, was produced by the reaction of thallium sulfate, Tl_2SO_4 , and

barium bis(hexafluoroisopropyl)phosphate, $\text{Ba}\{\text{OP}[\text{OCH}(\text{CF}_3)_2]_2\}$, in aqueous solution. This thallium compound is a crystalline solid which slowly decomposes above 200°C . Elemental analysis gave 11.69% C, 0.31% H, 33.53% Tl, and 3.98% P. Theoretically,

$\text{TlOP}[\text{OCH}(\text{CF}_3)_2]_2$ requires 11.97% C, 0.33% H, 33.98% Tl, and

5.15% P. Thallium hydroxide and $\text{HOP}(\text{OCH}_2\text{C}_2\text{F}_5)_2$ were made to react in carbon tetrachloride at reflux temperature to yield

thallium bis(pentafluoropropyl)phosphate, $\text{TlOP}(\text{OCH}_2\text{C}_2\text{F}_5)_2$, which is a white solid. This compound is soluble in diethyl

ether and melts at 226°C. Elemental analysis gave 13.20% C,

0.81% H, 5.77% P, and 28.40% Tl. Theory for $\text{TlOP}(\text{OCH}_2\text{C}_2\text{F}_5)_2$ is 11.32% C, 0.71% H, 5.48% P, and 36.14% Tl. There is some doubt about the thallium analysis on this sample because a check could not be run due to the sample size submitted for analysis. However, carbon, hydrogen, and phosphorus analyses are reasonable and the IR spectrum looks comparable to the other metal derivatives of $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$. No further work was done on these thallium phosphate diesters because of their high melting points.

Lead bis(pentafluoropropyl)phosphate, $\text{Pb}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_2$, was also prepared by the reaction of the hydroxide, $\text{Pb}(\text{OH})_2$, and the acid, $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$, in refluxing carbon tetrachloride.

The product, $\text{Pb}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_2$, is a white solid which decomposes without melting above 225°C. It is insoluble in CCl_4 and was washed with diethyl ether before analysis. This treatment removed the unreacted $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$; however, there may have been some unreacted $\text{Pb}(\text{OH})_2$ associated with the product as indicated by the elemental analysis. It gave 13.50% C, 0.78% H, 5.75% P, and 25.65% Pb, whereas,

$\text{Pb}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_2$ requires 15.51% C, 0.87% H, 6.67% P, and 22.29% Pb. In a similar manner and with similar results,

thorium bis(pentafluoropropyl)phosphate, $\text{Th}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_4$, was prepared. It is a white solid which melts above 285°C. By elemental analysis this material was found to be 15.49% C,

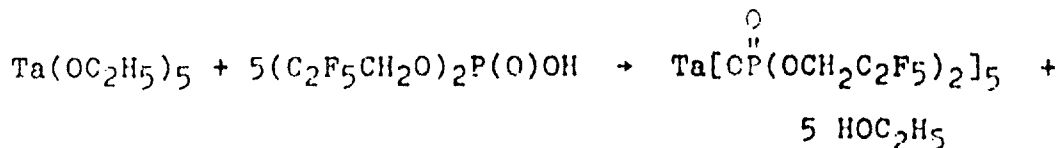
0.98% H, 7.80% P, and 18.50% Th. Theory for $\text{Th}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_4$ is 17.10% C, 0.96% H, 7.40% P, and 13.86% Th. Earlier in the program an attempt was made to prepare thorium bis(hexafluoro-

isopropyl)phosphate, $\text{Th}[\text{OP}(\text{OCH}(\text{CF}_3)_2)_2]_4$, by the reaction of

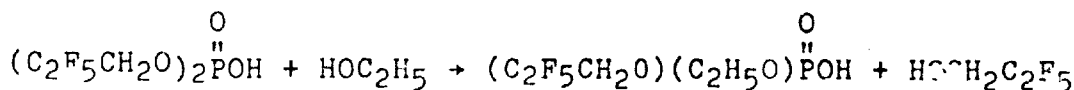
thorium sulfate, $\text{Th}(\text{SO}_4)_2$, and $\text{Ba}[\text{OP}(\text{OCH}(\text{CF}_3)_2)_2]_2$, in aqueous solution. However, the soluble white solid which was isolated was found to contain 8% Ba and only 0.01% Th.

The possibility of synthesizing heavy metal phosphate diesters by the reaction of metal alkoxides and an acid, $(\text{R}_f\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$ was also investigated. To prepare tantalum bis(pentafluoro-

propyl)phosphate, $\text{Ta}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_5$, $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$ were heated to 175°C . for four hours. The following equation represents the reaction:



In addition to $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$ were isolated from the reaction mixture. The white solid which remained after distilling off the above three products could not be identified by its IR spectrum. However, the solubility characteristics of this material in various solvents suggested that it was a mixture of products. The recovery of HOC_2H_5 indicated that the following side reaction had occurred:



No further work was done on this type of reaction because of the complexity of the reaction. Another attempt was made to

prepare $\text{Ta}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_5$ by the reaction of TaCl_5 and the silver salt of $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$ in diethyl ether. The results were similar to those of the $\text{Ta}(\text{OC}_2\text{H}_5)_5$ reaction in which a large number of products were obtained.

Bismuth trichloride, BiCl_3 , was also made to react with the silver salt of $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$ in diethyl ether, and the chief product of this reaction was the acid, $(\text{C}_2\text{F}_5\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$. Possibly, the hydrolysis of the BiCl_3 occurred and prevented

the formation of $\text{Bi}[\text{OP}(\text{OCH}_2\text{C}_2\text{F}_5)_2]_3$. The reaction of BiCl_3 and the silver salt of $[(\text{CF}_3)_2\text{CHO}]_2\text{P}(\text{O})\text{OH}$ in diethyl ether produced a white soluble solid which was isolated and dissolved in benzene in an attempt to recrystallize it. However, this solid would not deposit out of solution and when the solvent was evaporated in vacuo on a steam bath the product decomposed to a brown solid.

Finally, it was found that mercuric oxide, HgO , reacts with $(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$ in acetonitrile; however, the reaction was run on a small scale and no definite identification of products were made.

In summary, the reactions of $(C_2F_5CH_2O)_2P(O)OH$ and the hydroxides of thallium, lead, and thorium have produced metal phosphate diesters. Although the analytical data for these compounds are not exact, they do approach the theoretical values. If these compounds were recrystallized from suitable solvents, better data could be obtained. The IR spectra of these materials support their identity. As reported, the melting points of these compounds are all greater than $200^\circ C$. This indicates that these compounds are probably ionic salts, and minor changes in the fluoroalkoxy groups bonded to phosphorus would not produce liquid materials. Therefore, no further work was done on the phosphate diesters of lead, thorium, and thallium. It is possible that metals which form more covalent-type compounds will yield liquid phosphate diester derivatives. These metals would include hafnium, tantalum, bismuth, and mercury. Since hafnium and tantalum compounds would require four and five phosphate groups to be associated with them, it is questionable whether their densities would reach 2.5 g./cc. Thus, the efforts in this area should be devoted to the synthesis of bismuth and mercury phosphate diesters. Research is now in progress and should reveal if the phosphate diesters of these two metals will yield fluid materials.

C. HEAVY METAL β -DIKETONATES

Efforts in this area involved the synthesis of the fluorinated β -diketones and their subsequent reactions to form the metal complexes. The following four diketones were prepared: decafluoro-

2,4-heptandione, $CF_3\overset{\overset{O}{\parallel}}{C}CH_2\overset{\overset{O}{\parallel}}{C}CF_7$; octadecafluoro-2,4-undecandione, $CF_3\overset{\overset{O}{\parallel}}{C}CH_2\overset{\overset{O}{\parallel}}{C}C_7F_{15}$; heptafluoro-2,4-heptanedione, $CH_3\overset{\overset{O}{\parallel}}{C}CH_2\overset{\overset{O}{\parallel}}{C}CF_7$; and pentadecafluoro-2,4-undecandione, $CH_3\overset{\overset{O}{\parallel}}{C}CH_2\overset{\overset{O}{\parallel}}{C}C_7F_{15}$.

To prepare the above fluorinated β -diketones, the ethyl esters of heptafluorobutyric acid, $HOCC_3F_7$, and pentadecafluorooctanoic acid, $HOCC_8F_{15}$, were synthesized by the reactions of the acids and ethyl alcohol in the presence of concentrated sulfuric acid. After separation of the immiscible sulfuric acid and ester layers, neutralization, washing, and drying over sodium sulfate, the esters were distilled. Ethyl heptafluorobutyrate, $C_2H_5OCC_3F_7$, distills at $95^\circ-96^\circ C$., and ethyl pentadecafluorooctanoate, $C_2H_5OCC_8F_{15}$, distills at $165^\circ-170^\circ C$..

The synthesis of $CF_3\overset{\overset{O}{\parallel}}{C}CH_2\overset{\overset{O}{\parallel}}{C}CF_7$, essentially that of A. L. Henne et al., (14) involved the condensation of $C_2H_5OCC_3F_7$

with trifluoroacetone, $\text{CH}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$, in the presence of sodium ethoxide and diethyl ether. The diketone was isolated as the copper complex, $\text{Cu}(\text{C}_7\text{HO}_2\text{F}_{10})_2$, which is soluble in diethyl ether and distills at 110°C . and 0.16 mm. Hg in a Hickman still. Elemental analysis and IR spectrum indicated a small amount of impurity associated with the complex, probably the free β -diketone. Elemental analysis gave 26.12% C, 1.10% H, and 8.63% Cu, whereas $\text{Cu}(\text{C}_7\text{HO}_2\text{F}_{10})_2$ requires 24.81% C, 0.30% H, and 9.38% Cu. Its density at 23°C . is 1.73 g./cc. Moshier and Sievers (15) report $\text{Cu}(\text{C}_7\text{HO}_2\text{F}_{10})_2$ as a solid which melts at $73^\circ\text{--}83^\circ\text{C}$. and sublimates at 50°C . and 0.1 mm. Hg. Ethereal solutions of $\text{Cu}(\text{C}_7\text{HO}_2\text{F}_{10})_2$ yield the free β -diketone when treated with concentrated sulfuric acid or gaseous hydrogen sulfide. The sulfide method is cleaner and gives better yields. By this method

$\text{CF}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$ was obtained from the copper complex and purified by distillation at $100^\circ\text{--}103^\circ\text{C}$.

Octadecafluoro-2,11-undecandione was prepared by the reaction

of $\text{C}_2\text{H}_5\text{OCCF}_{15}$, $\text{CF}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_3$ and sodium methoxide in diethyl ether. After neutralization with dilute hydrochloric acid, washing and drying over sodium sulfate, distillation at $170^\circ\text{--}174^\circ\text{C}$. yielded a mixture of the diketone and unreacted ester. To separate these two, the mixture was treated with aqueous copper acetate to

yield the copper complex of $\text{CF}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_3$ which precipitated as a green solid. After recrystallization, elemental analysis and the IR spectrum identified the complex as the monohydrate, $\text{Cu}(\text{C}_{11}\text{HO}_2\text{F}_{18})_2 \cdot \text{H}_2\text{O}$. Analysis gave 25.00% C, 0.80% H, and 5.76% Cu: $\text{Cu}(\text{C}_{11}\text{HO}_2\text{F}_{18})_2 \cdot \text{H}_2\text{O}$ requires 24.1% C, 0.37% H, and 5.80% Cu. The free diketone was produced by the hydrogen sulfide treatment and distilled at 178°C .

Heptafluoro-2,4-heptanedione, and pentadecafluoro-2,4-undecanedione were prepared by the condensation of $\text{C}_2\text{H}_5\text{OCCF}_7$ and $\text{C}_2\text{H}_5\text{OCCF}_{15}$ with acetone in the presence of sodium methoxide and diethyl ether. Since these two diketones could be separated from the unreacted esters by distillation, the isolation procedures did not involve the copper complexes. The

heptanedione, $\text{CH}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_7$, distills at $135^\circ\text{--}140^\circ\text{C}$., and

$\text{CH}_3\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}_2\overset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CF}_{15}$ distills at $49^\circ\text{--}51^\circ\text{C}$. at 0.85 mm. Hg.

The metal complexes which were prepared from these diketones are listed in Table V. The thorium compound was

made by the reaction of ThCl_4 and $\text{CF}_3\overset{\text{O}}{\parallel}\text{CH}_2\overset{\text{O}}{\parallel}\text{CCF}_3$ in refluxing CCl_4 , and distilled in a micro still. However, there was poor separation of $\text{Th}(\text{C}_7\text{HO}_2\text{F}_{10})_4$ from the lower boiling fractions and this is shown in the elemental analysis. This was the only β -diketonate which is a liquid and its density is 1.897 g./cc. at 22°C. Since the density was so low, no further work was done on thorium diketonates. Plans to prepare hafnium diketonates were not followed because no significant increase in density for these compounds could be envisioned. It is interesting to note that the hafnium analog, $\text{Hf}(\text{C}_7\text{HO}_2\text{F}_{10})_4$, of $\text{Th}(\text{C}_7\text{HO}_2\text{F}_{10})_4$ has been reported (15), and it is a liquid which distills at 70°C. and 0.02 mm. Hg.

The thallium diketonates were prepared by the reaction of Tl_2CO_3 and the appropriate diketone in refluxing benzene. They are all yellow crystalline solids with relatively high melting points. Purification of $\text{TlC}_7\text{HO}_2\text{F}_{10}$ and $\text{TlC}_{11}\text{HO}_2\text{F}_{18}$ was achieved by vacuum sublimation, whereas $\text{TlC}_7\text{H}_4\text{O}_2\text{F}_7$ was recrystallized from a water-methanol mixture and $\text{TlC}_{11}\text{H}_4\text{O}_2\text{F}_{15}$ from a hexane-benzene mixture. The hexane-benzene mixture gave better results than the water-methanol mixture. Although these compounds are volatile and can be vacuum sublimed, their high melting points indicate that a liquid thallium β -diketonate will probably not be realized.

To obtain a high density liquid out of this class of compounds, it appears that the metal complex will have to have more than one, but less than four, fully fluorinated ligand groups associated with it. Thus, the greatest likelihood for success will lie with the synthesis of the metal β -diketonates of mercury, lead, bismuth, hafnium, thorium, and uranium. Hafnium and thorium are included because they form partially substituted β -diketone complexes of the type ML_2X_2 and ML_3X , where L is the diketone group and X represents a halide. Uranium forms UL_4 and UO_2L_2 complexes of which UO_2L_2 would be of greater interest to this project. Little is known of the mercury, lead and bismuth β -diketonates (16).

TABLE V
ANALYSIS AND PHYSICAL PROPERTIES OF METAL β -DIKETONATES

Compound	Analysis, Wt. %				Physical Properties		
	C	H	Tl	Th	M.P., °C.	B.P., °C./mm. Hg	Density g./cc.
$\text{Th}(\text{C}_7\text{HO}_2\text{F}_{10})_4$	24.35	0.73	---	15.40	---	88/0.009	1.897 at 22°C.
Theory	23.03	0.28	---	15.89			
$\text{TlC}_7\text{HO}_2\text{F}_{10}$	16.15	0.23	39.70	---	96-98	Sublimes at 85/0.01	---
Theory	16.44	0.20	39.96	---			
$\text{TlC}_{11}\text{HO}_2\text{F}_{18}$	18.60	0.18	28.58	---	103-104	Sublimes at 100/0.01	---
Theory	18.57	0.14	28.72	---			
$\text{TlC}_7\text{H}_4\text{O}_2\text{F}_7$	18.39	0.92	43.6	---	90.5-92	Sublimes at 90/0.02	---
Theory	18.39	0.88	44.67	---			
$\text{TlC}_{11}\text{H}_4\text{O}_2\text{F}_{15}$	19.78	0.58	31.40	---	131.5-133.5	---	---
Theory	20.09	0.61	31.08				

III. CONCLUSIONS

This research program has produced two compounds which meet the density requirement for use in a gyroscope. The first, is $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$, which is distillable and has a density of 2.598 g./cc. at 25°C. The second is $\text{TlOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$, which has not yet been purified, but the density of the crude product is 2.48 g./cc. at 23°C. Since distilled $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ slowly crystallizes at room temperature and does not completely liquefy until heated to 54°C., which is above the operating temperature of present gyroscopes, it is not known if this material will eventually be useful. On the assumption that it will be useful, work is in progress to determine its viscosity, thermal stability, corrosiveness and toxicity. It is expected that when $\text{TlOCH}_2(\text{CF}_2)_7\text{CF}_2\text{H}$ is purified its density will exceed 2.5 g./cc.

At present, the fluoroalkoxides of thallium offer the best chance of obtaining fluids with the needed densities. Future synthesis efforts should be directed to finding a fluoroalcohol which will yield a thallium fluoroalkoxide with a lower liquefaction point than that presently attained. Examples of alcohols which could possibly be used are: $\text{HOCH}_2\text{C}_7\text{F}_{15}$, $\text{HOCH}_2(\text{OC}_2\text{F}_4)_4\text{OC}_2\text{F}_5$ and perfluorinated alcohols, such as, $\text{HOC}(\text{CF}_3)_3$, $\text{HOC}(\text{CF}_3)_2\text{C}_2\text{F}_5$ and $[\text{HOC}(\text{CF}_3)_2]_2$.

Although fluids with densities of only 2.0 g./cc. were obtained with hafnium and tantalum fluoroalkoxides, perfluorinated alkoxides of hafnium could yield fluids of higher densities. Therefore, it is recommended that work in this area continue with emphasis upon producing hafnium perfluoroalkoxides. Synthesis methods other than that which uses ammonia should also be investigated.

From data in the literature and that obtained during this research program, it can be concluded that the synthesis of fluoroalkoxides of cerium, thorium, lead and mercury will not yield useful products for this application.

The data from the work on the heavy metal phosphate diesters are not as precise as that for the fluoroalkoxides. However, the results which were obtained give an indication of the future direction of the work. The hydrogen phosphate diesters $\text{HO}(\text{O})\text{P}(\text{OCH}_2\text{R})_2$ are fairly strong acids and most of their metal derivatives will have considerable ionic character resulting in high melting solids. This is verified by the work on the lead, thallium and thorium phosphate diesters. Metals, such as bismuth and mercury, may form more covalent type compounds and it is possible that their phosphate diesters will be fluids. This should be investigated. If bismuth

and mercury form solid phosphate diesters but with melting points significantly lower than those already prepared, then their phosphate diesters of longer chain fluoroalkyl groups should be prepared as a means of obtaining materials of lower melting points.

Another possible method of obtaining liquids from this class of compounds would be to prepare phosphate diesters with mixed

fluoroalkyl groups, such as $\text{HOP} \begin{array}{l} \text{O} \\ \text{OCH}_2\text{CF}_3 \\ \text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H} \end{array}$

It is also possible to prepare phosphate diesters with perfluorinated alkyl groups, i.e., $[(\text{CF}_3)_3\text{CO}]_2\text{P}(\text{O})\text{OH}$, and in this case the hafnium derivative may be of interest.

Liquid thorium and hafnium β -diketonates can be prepared, but their densities will not meet the objectives of this work. Thallium β -diketonates are solids, and it does not appear that liquid chelates of this metal can be prepared. As stated in the previous Section, the greatest likelihood of obtaining a high density liquid from this class of compounds appears to be with heavy metals which can accommodate two or three chelate groups. Partially substituted hafnium β -diketonates, HfCl_2L_2 and HfClL_3 , and uranyl complexes, UO_2L_2 , are future areas of research. If the hafnium complexes look promising, then the work will be extended to include thorium. It is possible that lead(II) β -diketonates can also be prepared; however, there is very little evidence for the existence of mercury and bismuth chelates of this type (16), and no work on these compounds is projected.

IV. EXPERIMENTAL

A. MATERIALS

Hafnium tetrachloride and tantalum pentachloride were obtained from Alfa Inorganics, Incorporated, and were used without further purification. Thallium hydroxide was purchased from City Chemical Corporation.

Trifluoroethanol, pentafluoropropanol, heptafluorobutanol, dodecafluoroheptanol, hexadecafluorononol, dodecafluoro-2-methyl-2-octanol, trifluoroacetone, heptafluorobutyric acid and pentadecafluorooctanoic acid were purchased from Columbia Organic Chemicals Company.

Hexafluoro-2-propanol was purchased from Hynes Chemical Research Corporation.

B. PREPARATIONS

1. Preparation of Hafnium Fluoroalkoxides

The method of D. C. Bradley et al.(4) was used to prepare these compounds. However, hafnium tetrachloride instead of di-pyridinium hafnium hexachloride was used as the starting material. Two examples of these preparations are given below.

Hafnium trifluoroethoxide was prepared from 30 g. of hafnium tetrachloride, 37.5 g. of trifluoroethanol, and excess ammonia in 300 ml. of benzene. The white solid product (12 g.) was purified by sublimation at 95°C. and 0.005 mm. Hg. It had a melting point of 106°-107°C. Elemental analysis verified the composition.

The reaction of 13.5 g. of hafnium tetrachloride, 56 g. of dodecafluoroheptanol and excess ammonia in 300 ml. of benzene produced hafnium dodecafluoroheptoxide. This viscous, brown product was distilled at 245°C. and 0.003 mm. Hg. During the distillation some thermal decomposition occurred and a large portion of the sample was lost. Approximately 10 g. of dark brown, viscous product was isolated and its composition was verified by elemental analysis.

2. Preparation of Tantalum Ethoxide

This compound was prepared according to the method of D. C. Bradley et al.(5). The liquid product was purified by distillation at 126°C. and 0.11 mm. Hg. The reported boiling point is 147°C. at 0.2 mm. Hg. From 60 g. of tantalum pentachloride, 150 ml. of ethanol and an excess of ammonia in 1200 ml. of benzene, 53 g. of tantalum ethoxide was isolated.

3. Preparation of Tantalum Trifluoroethoxide

The above method was used to prepare tantalum trifluoroethoxide from tantalum pentachloride (25 g.) and 40 g. of trifluoroethanol in 300 ml. of benzene. After filtration and evaporation of the solvent, the crude product was a white mush of the alkoxide and alcohol. Repeated sublimation of a 5 g. sample at 100°C. and 0.02 mm. Hg yielded 4.8 g. of the pure tantalum trifluoroethoxide which melted at 95°C. Elemental analysis verified that this material was the trifluoroethoxide.

4. Attempted Preparation of Tantalum Dodecafluoroheptoxide and Tantalum Dodecafluoro-2-methyl-2-octoxide

In a dry box 8 g. of tantalum ethoxide, 35 g. of dodecafluoroheptanol and 100 ml. of benzene were mixed in a 250 ml. flask. The flask was then set up with a Dean-Stark trap and condenser with a nitrogen inlet so that the reaction could be run under a nitrogen atmosphere. The reaction mixture was heated to reflux and the benzene-ethanol azeotropic mixture which distilled out was collected in the trap. An IR spectrum of the distillate proved that ethanol was produced in the reaction. The distillation was continued until almost all of the benzene had been removed from the reaction. The remaining liquid was transferred to a molecular still and pumped on until all of the solvent was removed. Distillation of the product (14.7 g.) was accomplished at 250°C. and <0.001 mm. Hg. Elemental analysis and proton NMR spectroscopy proved that the yellow-brown liquid product was $\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4[\text{OC}_2\text{H}_5]$.

In a similar manner, $\text{Ta}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_3[\text{OC}_2\text{H}_5]_2$ was isolated as the product of the reaction of 8 g. of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and 38 g. of $\text{HOC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}$. Brown, liquid $\text{Ta}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_3[\text{OC}_2\text{H}_5]_2$ distilled at 250°C. and 0.005 mm. Hg. Its composition was determined by elemental analysis and its proton NMR spectrum.

In the same manner, 14.7 g. of $\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4[\text{OC}_2\text{H}_5]$ and 9.5 g. of $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ were made to react in 100 ml. of benzene at reflux temperature for 12 hours. The product was distilled at 260°C. and 0.001 mm. Hg, and proton NMR spectroscopy proved that it was a mixture of tantalum compounds with a 6:1 ratio of $-\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ groups to $-\text{OC}_2\text{H}_5$ groups.

5. Attempted Preparation of Thorium Dodecafluoroheptoxide

The method of preparing thorium dodecafluoroheptoxide was similar to that of D. C. Bradley for synthesizing the thorium primary alkoxides (7). A 250 ml. flask was fitted with a Soxhlet extractor and condenser with a nitrogen inlet. The flask was charged with 125 ml. of isopropanol and 8 g. of thorium tetrachloride and the contents were stirred until a clear solution was obtained. The

Soxhlet extractor was then loaded with 2 g. of sodium metal in a glass thimble, and the metal was extracted into the reaction flask as sodium isopropoxide. After complete extraction, the reaction mixture was filtered under nitrogen and the solvent was removed from the filtrate by vacuum evaporation. The white solid which remained from this desolvation was treated with 300 ml. of benzene and 10 g. of dodecafluoroheptanol. This mixture was heated to reflux temperature and the benzene-isopropanol azeotropic mixture which distilled out was collected in a Dean-Stark trap. The volume of the reaction mixture was reduced to ~20 ml. by this method, after which time it was cooled. Upon cooling, a white crystalline material deposited out of solution. These crystals were collected by filtration and washed with hexane in a dry box. Elemental analysis indicated that this material was mainly sodium dodecafluoroheptoxide and not thorium dodecafluoroheptoxide.

6. Preparation of Thorium Hexadecafluorononoxide

A 250 ml. flask was equipped with a stirrer, nitrogen inlet and addition funnel. The flask was charged with 100 ml. of diethyl ether and 1.5 g. of sodium metal. A solution of 29 g. of hexadecafluorononol in ~50 ml. of ether was then added dropwise. After all of the sodium had reacted, a slurry of 10 g. of thorium tetrachloride tetraisopropylate in ether was added. This mixture was stirred overnight at room temperature. The ether was removed by vacuum evaporation, and 100 ml. of benzene was added to the solids which remained. This was heated to reflux and filtered under nitrogen. Upon cooling the filtrate, 12 g. of white crystals deposited out of solution, were collected by filtration, and vacuum dried. Elemental analysis indicated that this material was thorium hexadecafluorononoxide with ~3% sodium in it.

7. Preparation of Dipyridinium Cerium Hexachloride

This material was prepared by the procedure of D. C. Bradley et al. (8). Cerium sulfate was used as the starting material instead of cerium ammonium sulfate. The yield of product was 52 g. from 50 g. of cerium sulfate.

8. Attempted Preparation of Cerium Dodecafluoroheptoxide

An attempt was made to prepare this compound by the method of D. C. Bradley (8) for preparing cerium primary alkoxides. A mixture of 10 g. of dipyridinium cerium hexachloride and 30 g. of dodecafluoroheptanol in 100 ml. of benzene at room temperature was treated with ammonia for two hours. After filtration and evaporation of the benzene in vacuo, the excess alcohol was distilled from the brown, viscous product at 34°C. and 0.1 mm. Hg. Continued distillation only produced more alcohol, and it appeared that the product was decomposing. Upon cooling the brown product turned

to a glassy material. In a dry box, attempts were made to crystallize this material in benzene, hexane, acetone, ether and a benzene-hexane mixture; however, these were unsuccessful. A second preparation yielded the same results.

9. Preparation of Thallium Fluoroalkoxides

A mixture of 5 g. of thallium hydroxide and 40 ml. of pentafluoropropanol was allowed to stir overnight in a sealed flask at room temperature. The reaction mixture was filtered under nitrogen to remove the unreacted thallium hydroxide. Excess alcohol was removed from the filtrate by vacuum evaporation and the white crystalline solid which remained was identified as thallium pentafluoropropoxide by elemental analysis and IR spectroscopy. This material had a diffuse melting point beginning at 50°C.

In a similar manner, 5.3 g. of thallium trifluoroethoxide was synthesized from 6.5 g. of thallium hydroxide and 10 g. of trifluoroethanol. Thallium trifluoroethoxide sublimes at 40°C. and 0.04 mm. Hg, and has a diffuse melting point beginning at ~93°C.

Similarly, 10 g. of thallium hydroxide and ~55 ml. of $\text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ were made to react at room temperature in a 100 ml. flask. After removal of unreacted hydroxide the excess alcohol was evaporated off in vacuo at 55°C. to produce 24.6 g. of yellow liquid. Elemental analysis indicated that this material had the following composition: $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H} \cdot 0.43 \text{HOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$. After vacuum pumping for twelve days at room temperature to remove the unreacted alcohol the sample was reduced to 16.6 g. Since the elemental analysis of this material varied from the theoretical values for $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$, it was transferred to a Nester-Faust molecular still. It was found that $\text{TlOCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$ can be purified by molecular distillation at 200°C. and <0.001 mm. Hg with very little thermal decomposition.

10. Attempted Preparation of Lead Trifluoroethoxide

A 150 ml. flask was charged with 24 g. of lead hydroxide and 23 g. of trifluoroethanol. This mixture was heated to reflux for 16 hours and filtered. The solids were washed with benzene; however, no products were recovered from these washings. An IR spectrum of the solids showed the absence of any fluorocarbon product. The filtrate was found to contain only unreacted trifluoroethanol. It was concluded that lead hydroxide and trifluoroethanol do not react at the above described conditions.

11. Preparation of Lead Dodecafluoroheptoxide

Lead nitrate (10 g.) in 100 ml. of water was treated with 2.4 g. of sodium hydroxide in 25 ml. of water. The lead hydroxide

which precipitated was collected, washed twice with water and transferred to a 250 ml. round bottom flask. Benzene (200 ml.) and 20 g. of dodecafluoroheptanol were added and the flask was equipped with a Dean-Stark trap and condenser. Under nitrogen the mixture was refluxed for ten days on a steam bath. Unreacted lead hydroxide was removed by filtration and the benzene and unreacted alcohol were evaporated in vacuo to produce a white mushy solid. This was vacuum dried at 55°C. for five days. Yield was 7 g. of a white solid which was identified by the IR spectrum and elemental analysis.

12. Attempted Preparation of Mercuric Dodecafluoroheptoxide

A three-neck, 500 ml. flask was equipped with a stirrer, condenser with a nitrogen inlet, and an addition funnel. The flask was charged with 70 ml. of benzene and 2 g. of sodium metal, and 30 g. of dodecafluoroheptanol were added dropwise from the funnel. After complete reaction of the metal, the benzene was evaporated off and 14.3 g. of mercuric acetate in 200 ml. of methanol was added. The mixing of these reactants immediately produced a yellow solid. After refluxing for two hours, the solids were removed by filtration under nitrogen. The yellow solid appeared to be mercuric oxide. The filtrate was evaporated to dryness and produced a white solid which proved to be mercuric acetate. A small amount of the fluoroalcohol was also isolated from the filtrate.

In another attempt to prepare mercuric dodecafluoroheptoxide, 2.5 g. of mercuric acetate and 15 g. of dodecafluoroheptanol were heated to 100°C. for two hours in a 50 ml. flask with a condenser and nitrogen inlet. The mixture was then cooled and the volatile fraction was pumped off and identified as dodecafluoroheptanol by its IR spectrum. The remaining solid material was identified as the starting mercury compound by its IR spectrum.

13. Preparation of the bis(Fluoroalkyl) Hydrogen Phosphates

The following procedure is an example for the preparations of bis(pentafluoropropyl) hydrogen phosphate, bis(hexafluoroisopropyl) hydrogen phosphate and bis(heptafluorobutyl) hydrogen phosphate.

A three-neck, 250 ml. flask with stirrer, condenser and addition funnel was charged with 10 g. of phosphorus pentoxide and 130 ml. of hexane. Pentafluoropropanol (42.2 g.) was added dropwise. During the alcohol addition the reaction mixture was kept at 0°C. by means of an ice bath. As the alcohol and phosphorus pentoxide reacted two layers were formed: hexane forms the upper layer. After complete addition of the alcohol, the mixture was heated to the reflux temperature of hexane for three hours. Upon cooling, the two layers were either separated by vacuum evaporation of the solvent or by means of a separatory funnel. The product was freed of unreacted alcohol by vacuum evaporation, and the product was purified by molecular distillation. The yield was 18.7 g.

The boiling points of these phosphates are: bis(pentafluoropropyl) hydrogen phosphate, 190°C. and 0.02 mm. Hg; bis(hexafluoroisopropyl) hydrogen phosphate, 180°C. and 1.0 mm. Hg; and bis-(heptafluorobutyl) hydrogen phosphate, 205°C. and 0.001 mm. Hg.

An example of the preparation of a hydrogen phosphate diester by the reaction of phosphoryl chloride and a fluoroalcohol is given below.

A 2-liter flask was fitted with an addition funnel, stirrer, and nitrogen inlet to allow the reaction to be run in a nitrogen atmosphere. The flask was charged with 40 g. of phosphoryl chloride and 250 ml. of hexane. This mixture was cooled in an ice bath, and 78.5 g. of pentafluoropropanol and 41 g. of pyridine were slowly added over a period of 1.5 hours. After allowing to warm to room temperature, the mixture was filtered under nitrogen and the hexane was distilled off at atmospheric pressure. The remaining liquid (59.6 g.) was distilled at 40°C. and 0.3 mm. Hg. Elemental analysis proved that this compound was bis(pentafluoropropyl) chlorophosphate.

This chlorophosphate was then hydrolyzed with an aqueous solution of 6.1 g. of sodium hydroxide. The water was evaporated off and the precipitated sodium chloride was filtered off. The product, bis(pentafluoropropyl) hydrogen phosphate, was then purified by molecular distillation at 190°C. and 0.02 mm. Hg.

14. Preparation of Thallium bis(Hexafluoroisopropyl) Phosphate

An aqueous solution of 1 g. of barium hydroxide octahydrate in 30 ml. of water was treated with 2.5 g. of bis(hexafluoroisopropyl) hydrogen phosphate to prepare the barium salt of this acid. This solution was then treated with an aqueous solution of 1.6 g. of thallium sulfate. The barium sulfate which precipitated was filtered off, and the filtrate was evaporated to dryness in vacuo to produce a white solid. This material was dissolved in acetone and refiltered. Vacuum evaporation of the acetone produced a white solid which had a melting point greater than 200°C. Elemental analysis proved that this substance was thallium bis(hexafluoroisopropyl) phosphate.

15. Attempted Preparation of Bismuth bis(Hexafluoroisopropyl) Phosphate

A solution of 3.8 g. of bis(hexafluoroisopropyl) hydrogen phosphate in 100 ml. of water was neutralized with aqueous sodium hydroxide. This solution was then treated with 1.6 g. of silver nitrate in 25 ml. of water. After stirring for fifteen minutes the mixture was filtered and evaporated to dryness in vacuo. The solids which remained were extracted with diethyl ether to dissolve the silver bis(hexafluoroisopropyl) phosphate. Bismuth trichloride

(4.5 g.) in 25 ml. of diethyl ether was added to the silver salt and the white precipitate which formed was filtered off. The ether solution was evaporated to dryness and the solids which remained were dissolved in benzene in an attempt to recrystallize. Upon cooling no crystals formed so the benzene was vacuum evaporated on a steam bath. At this temperature the product decomposed.

16. Preparation of Lead bis(Pentafluoropropyl) Phosphate

To a 100 ml. flask were added 1.8 g. of lead hydroxide, 80 ml. of carbon tetrachloride and 5 g. of bis(pentafluoropropyl) hydrogen phosphate. The mixture was refluxed over a week-end, cooled and filtered. The insoluble material (4.4 g.) was collected, washed with diethyl ether, and dried in vacuo. Elemental analysis and infrared spectroscopy proved this material to be lead bis(pentafluoropropyl) phosphate, which decomposes above 225°C.

17. Preparation of Thorium bis(Pentafluoropropyl) Phosphate

Thorium bis(pentafluoropropyl) phosphate was prepared in the manner which is described for lead bis(pentafluoropropyl) phosphate.

18. Preparation of Thallium bis(Pentafluoropropyl) Phosphate

This material was prepared in the manner which is described for lead bis(pentafluoropropyl) phosphate. However, this thallium compound is soluble in diethyl ether.

19. Preparation of the Ethyl Esters of Perfluorocarboxylic Acids

Heptafluorobutyric acid was esterified by treating 200 g. of this acid with 250 ml. of ethyl alcohol and 100 ml. of concentrated sulfuric acid. After stirring at room temperature for 48 hours, the sulfuric acid-ester layers were separated. The ester was then washed with water, aqueous sodium bicarbonate, and finally water again. Diethyl ether was added and the solution was dried over sodium sulfate. After filtration, the solution was distilled to isolate the ester. Ethyl heptafluorobutyrate boils at 95°-96°C., and was synthesized in 81% yield based on the acid.

Ethyl pentadecafluorooctanoate was prepared in 82% yield in a similar manner and boils at 169-170°C.

20. Preparation of Decafluoro-2,4-heptanedione

The condensation of ethyl heptafluorobutyrate with trifluoroacetone and the isolation of decafluoro-2,4-heptanedione was accomplished according to the method of Henne et al. (14) for preparing fluorinated diketones. Decafluoro-2,4-heptanedione distills at 99-105°C.

21. Preparation of Octadecafluoro-2,4-Undecanedione

The method of Moshier and Sievers (15) for preparing fluorinated diketones was used. Ethyl pentadecafluorooctanoate and trifluoroacetone were condensed in the presence of sodium methoxide. Since octadecafluoro-2,4-undecanedione could not be separated from unreacted ethyl pentadecafluorooctanoate by distillation, the isolation procedure of Henne et al. was used (14). Octadecafluoro-2,4-undecanedione distills at 178°C.

22. Preparation of Heptafluoro-2,4-heptanedione and Pentadecafluoro-2,4-undecanedione

The method of Moshier and Sievers (15) was used for preparing these β -diketones. Heptafluoro-2,4-heptanedione was made from 22.1 g. of sodium methoxide, 90 g. of ethyl heptafluorobutyrate and 21.8 g. of acetone in 50 ml. of diethyl ether. This diketone was purified by distillation at 135-140°C., and identified by its IR spectrum. Pentadecafluoro-2,4-undecanedione was prepared from 11.5 g. of sodium methoxide, 86 g. of ethyl pentadecafluorooctanoate and 11.3 g. of acetone in 50 ml. of diethyl ether. Purification was achieved by distillation at 49-51°C. and 0.85 mm. Hg. The product was identified by its IR spectrum.

23. Preparation of Thorium tetrakis(Decafluoro-2,4-heptanedionate)

A general method as mentioned by Morris et al. (17) was used to prepare this compound. A 50 ml., two-neck flask with a magnetic stirrer was charged with 4 g. of thorium tetrachloride and 25 ml. of carbon tetrachloride in a dry box. The flask was brought out and equipped with a condenser and addition funnel. The heptanedione (15 g.) was added dropwise and the mixture was refluxed for one hour. After cooling to room temperature, the mixture was filtered and the solvent removed by vacuum evaporation. Thorium tetrakis(decafluoro-2,4-heptanedionate) was isolated by distillation at 88°C. and 0.009 mm. Hg and identified by elemental analysis and IR spectrum. Yield was 8.6 g.

24. Preparation of the Thallium Fluoro- β -diketonates

The following is an example of the general method used to prepare the thallium diketonates by the reaction of thallium carbonate and the diketone in benzene.

A 50 ml. two-neck flask with a magnetic stirrer, condenser and addition funnel was charged with 9 g. of thallium carbonate and 25 ml. of benzene. To this were added dropwise 12 g. of decafluoro-2,4-heptanedione and the mixture was refluxed for one hour. After

filtration, the benzene was vacuum evaporated to yield an orange solid. This was purified by vacuum sublimation at 85°C. and 0.01 mm. Hg. The yield was 14.1 g. of thallium decafluoro-2,4-heptanedionate which was identified by elemental analysis and IR.

The preparation of the following diketonates is briefly described below:

- (i) Thallium octadecafluoro-2,4-undecanedionate:
13.1 g. from 6.8 g. of thallium carbonate and
15.8 g. of octadecafluoro-2,4-undecanedione.
Purified by sublimation at 100°C. and 0.01
mm. Hg.
- (ii) Thallium heptafluoro-2,4-heptanedionate:
10.3 g. from 6.0 g. of thallium carbonate and
6.54 g. of heptafluoro-2,4-heptanedione. Purified
by recrystallization from water-methanol
mixture.
- (iii) Thallium pentadecafluoro-2,4-undecanedionate:
13.4 g. from 5.0 g. of thallium carbonate and
9.70 g. of pentadecafluoro-2,4-undecanedione.
Purified by recrystallization from benzene-
hexane mixture.

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VI. APPENDIX

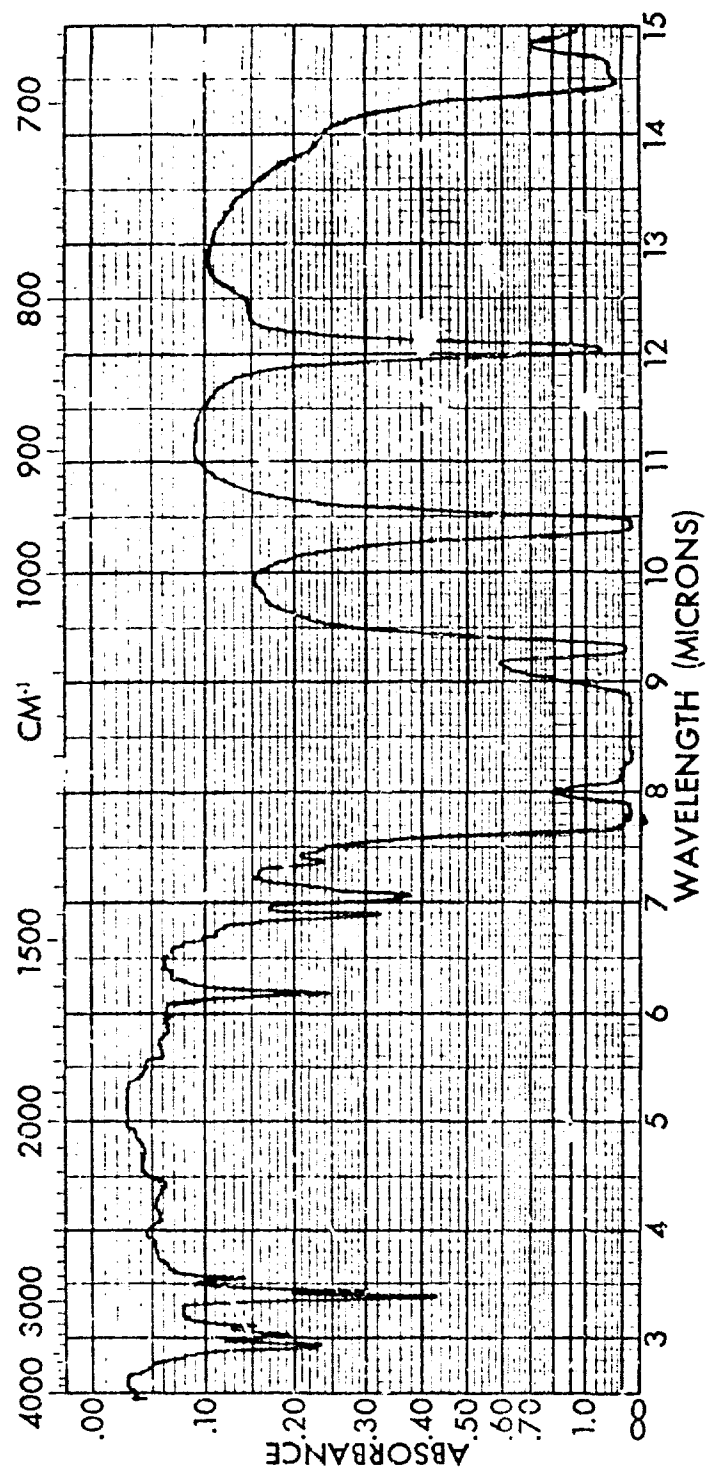


Fig. 1 - Infrared Spectrum of Hafnium Trifluoroethoxide
(Solid, Split Mull)

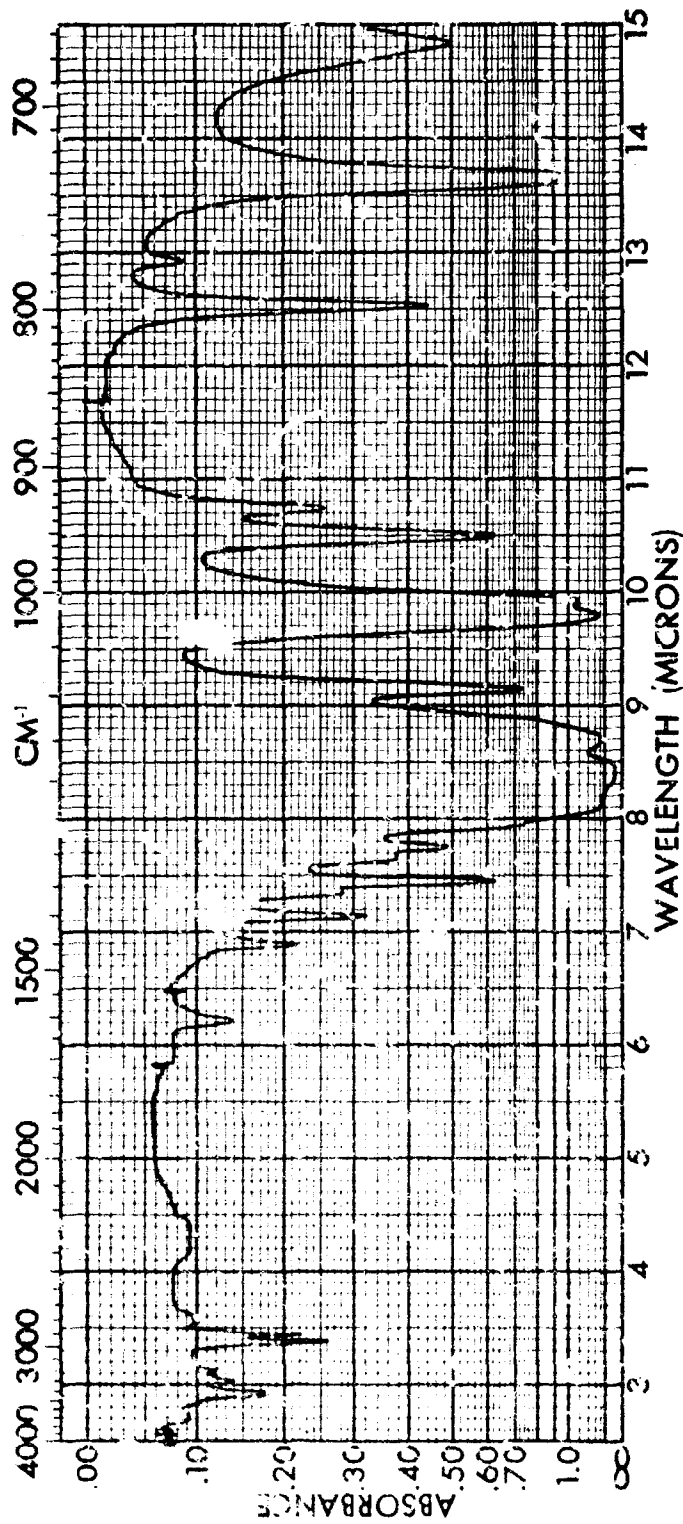


Fig. 2 - Infrared Spectrum of Hafnium Pentafluoropropoxide
(Solid, Split Mull)

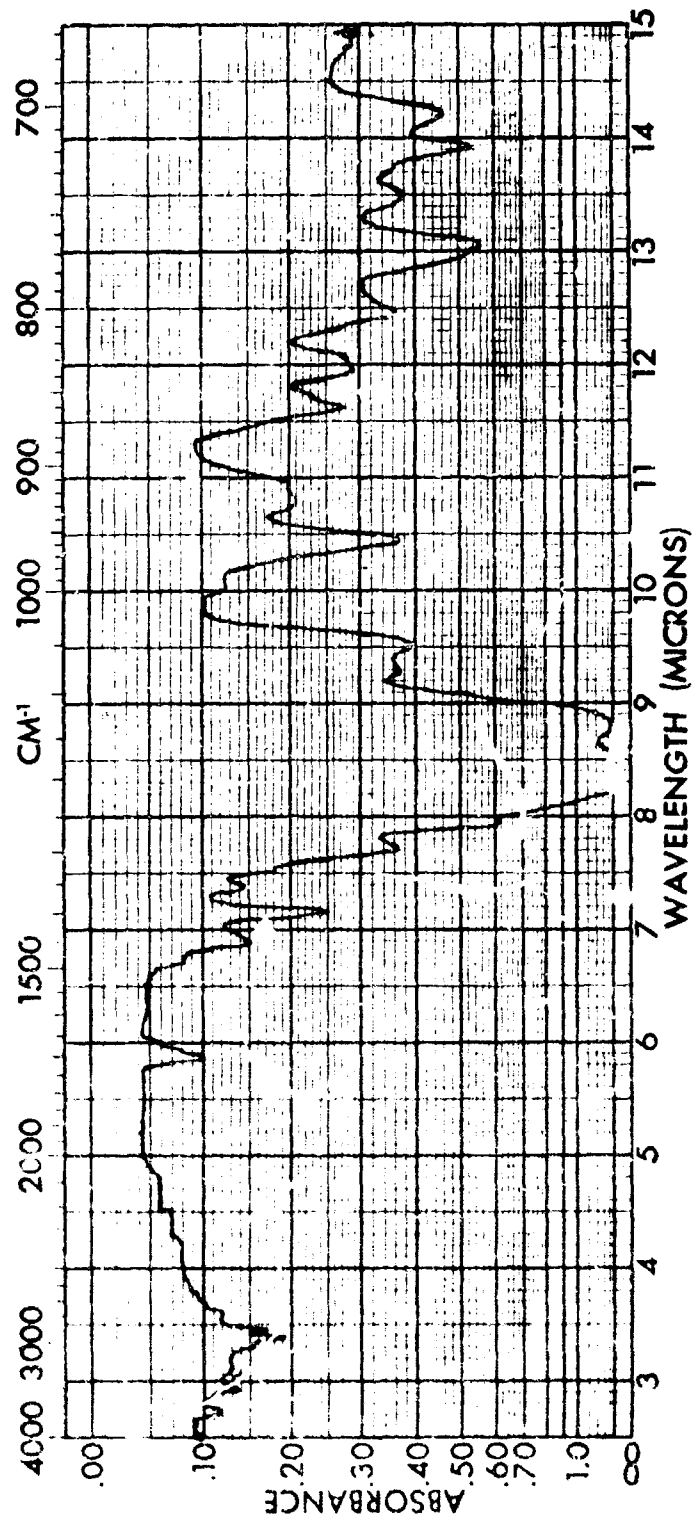


Fig. 3 - Infrared Spectrum of Hafnium Dodecafluoroheptoxide
(Liquid, Thin Film)

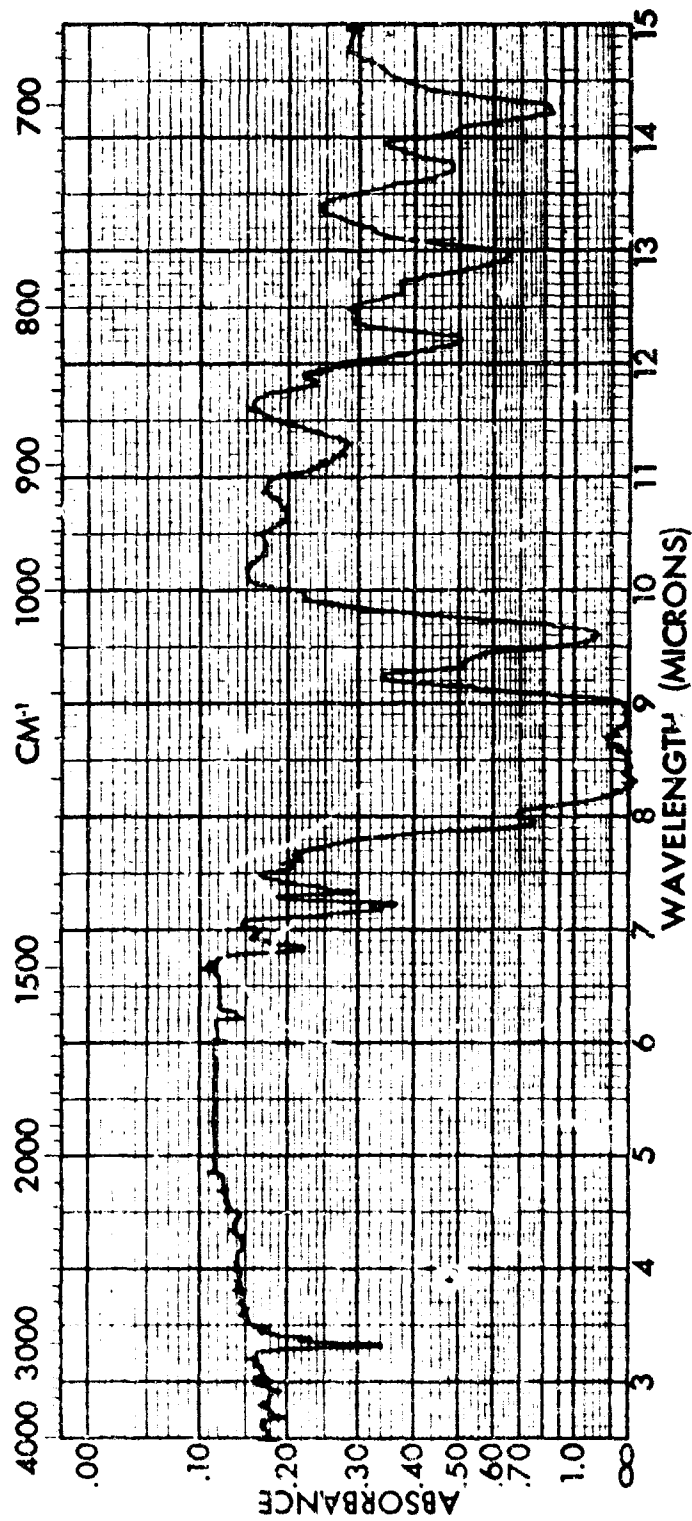


Fig. 4 - Infrared Spectrum of Hafnium Dodecafluoro-2-Methyl-2-Octoxide
(Liquid, Thin Film)

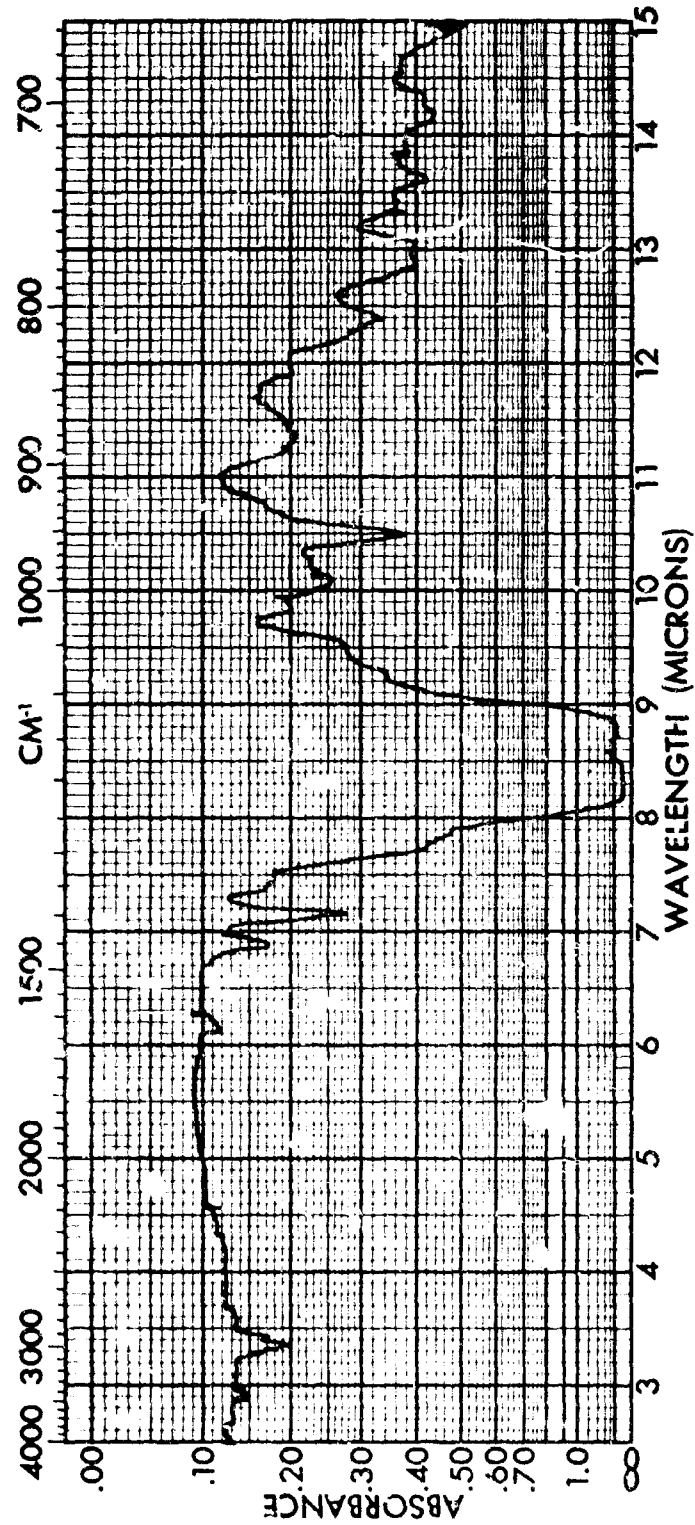


Fig. 5 - Infrared Spectrum of Hafnium Hexadecafluorononoxide
(Liquid, Thin Film)

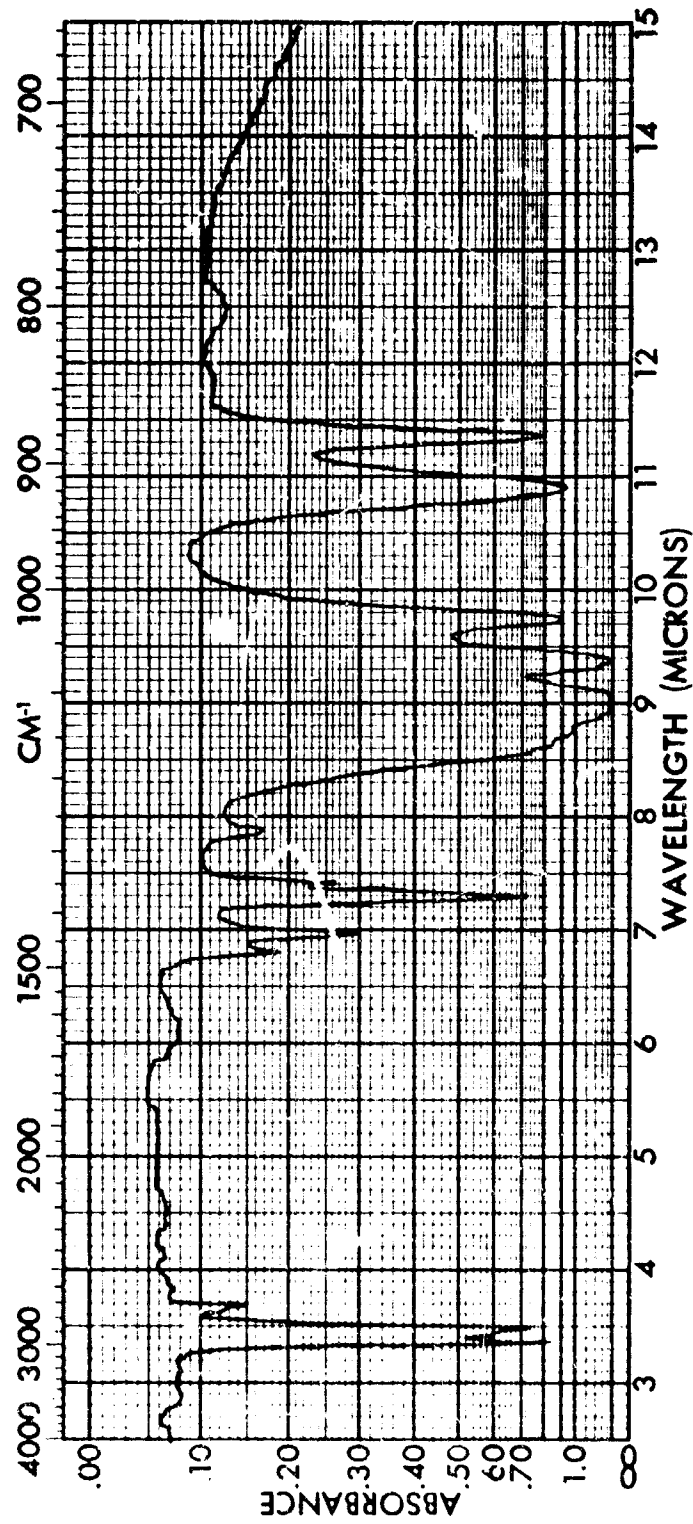


Fig. 6 - Infrared Spectrum of Tantalum Ethoxide
(Liquid, Thin Film)

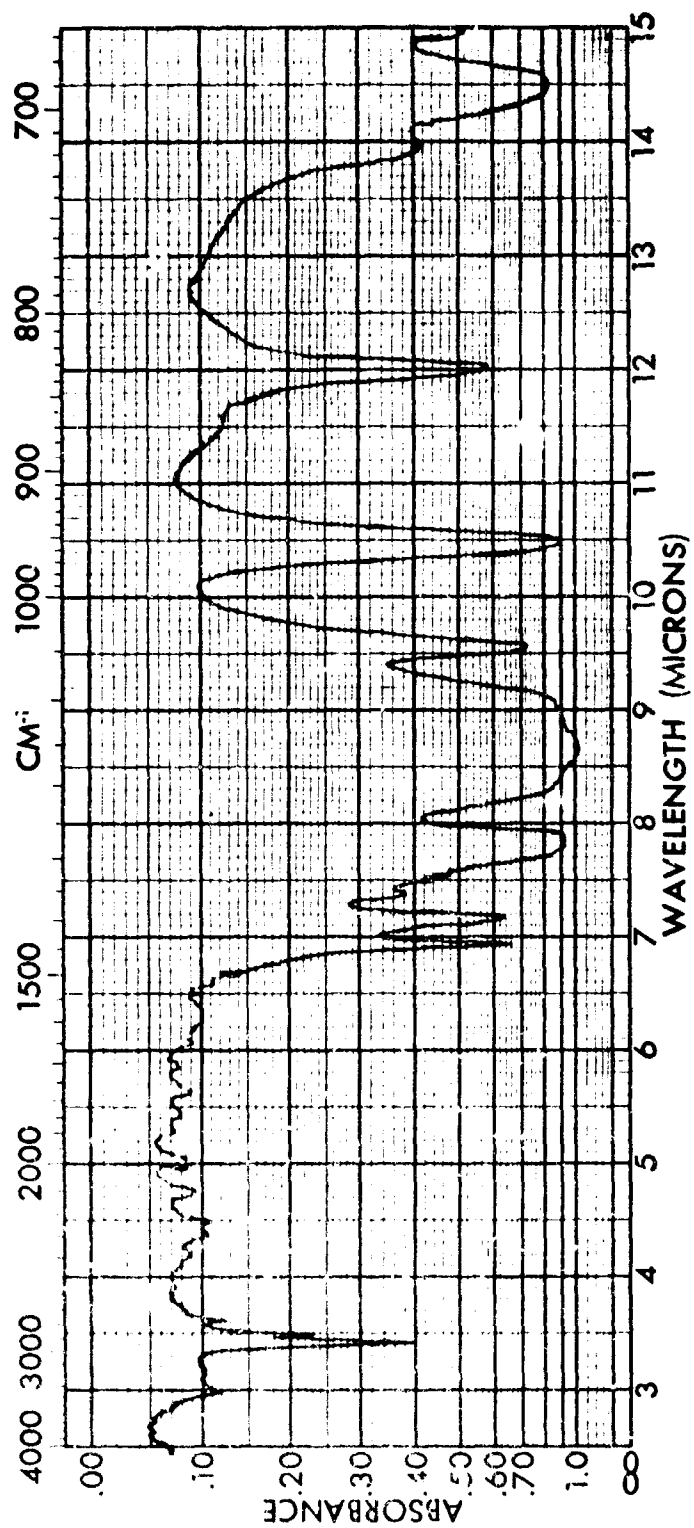


Fig. 7 - Infrared Spectrum of Tantalum Trifluoroethoxide
(Solid, Split Mull)

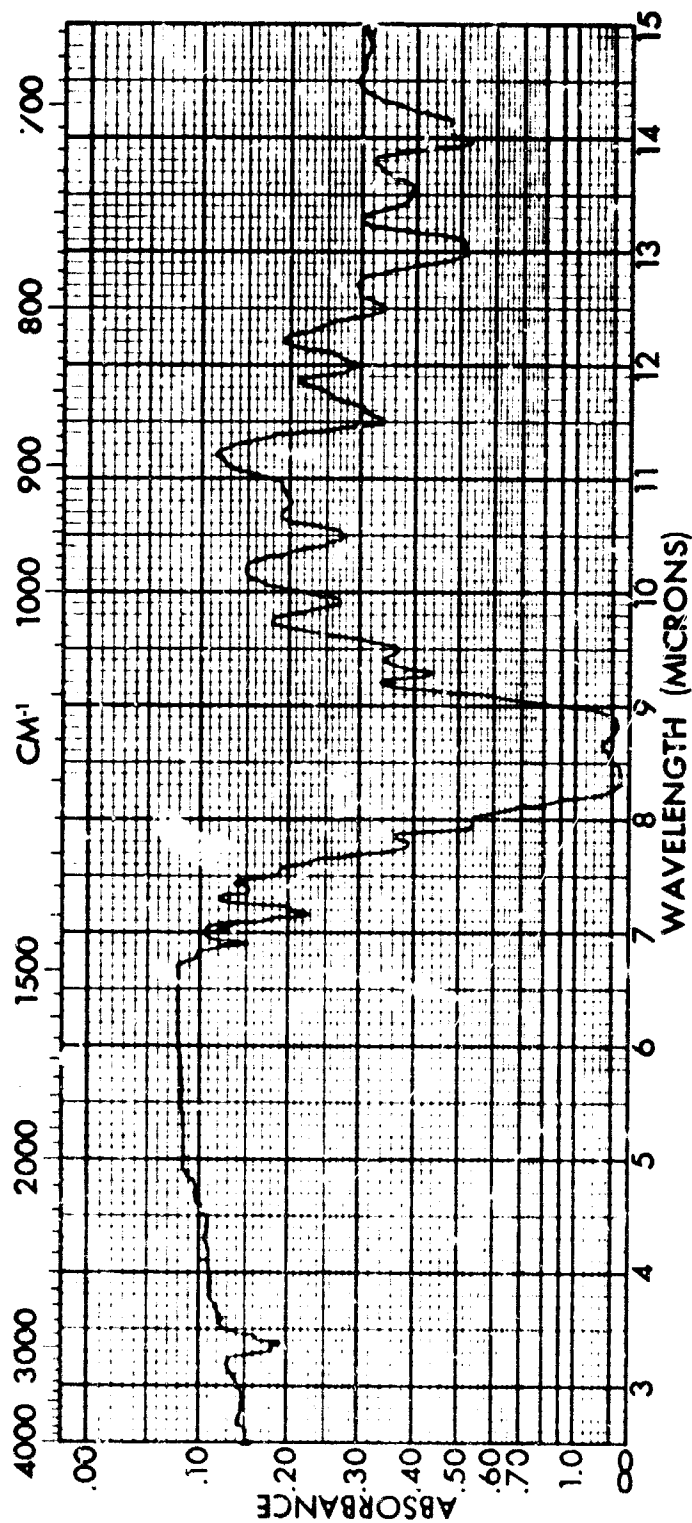


Fig. 2 - Infrared Spectrum of $\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_4[\text{OC}_2\text{H}_5]$
(Liquid, Thin Film)

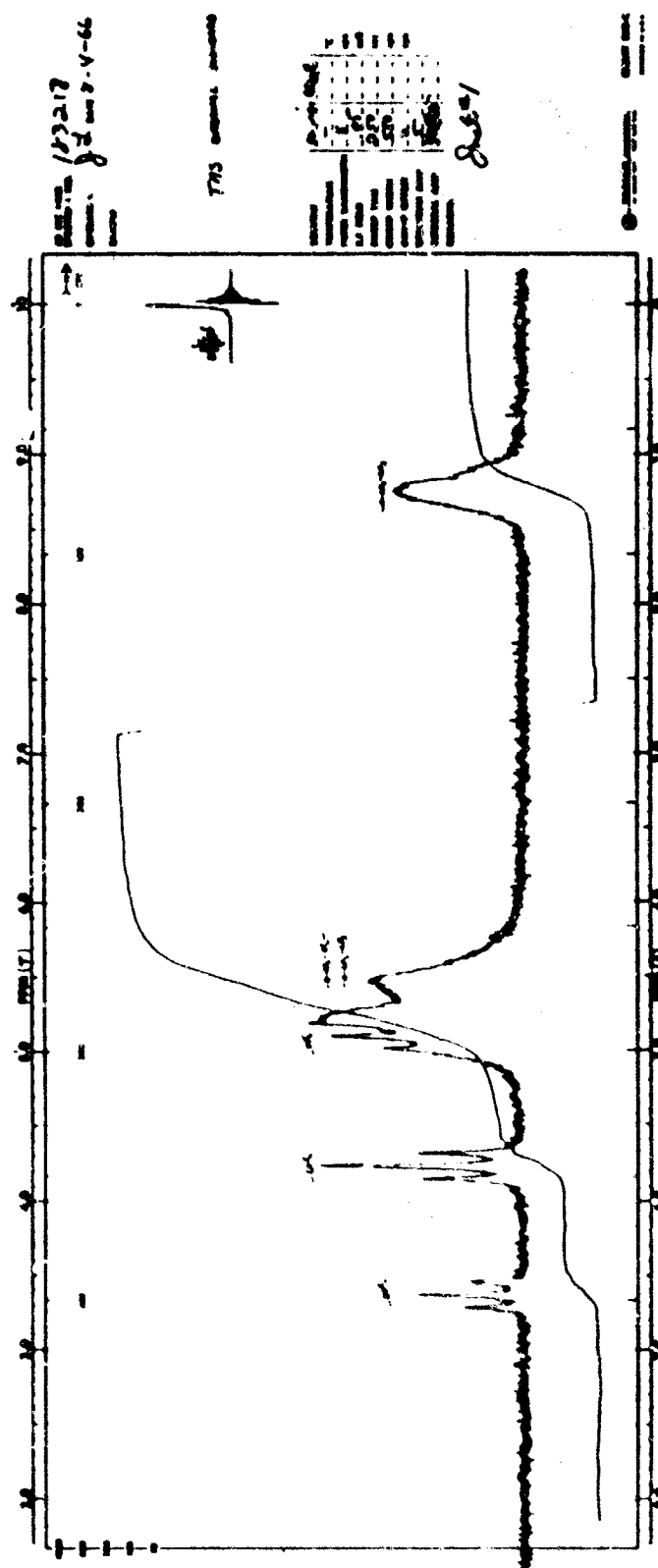


Fig. 9 - Proton Nuclear Magnetic Resonance Spectrum of
 $\text{Ta}[\text{OCH}_2(\text{CF}_3)_5\text{CF}_2\text{H}]_4(\text{OC}_2\text{H}_5)$

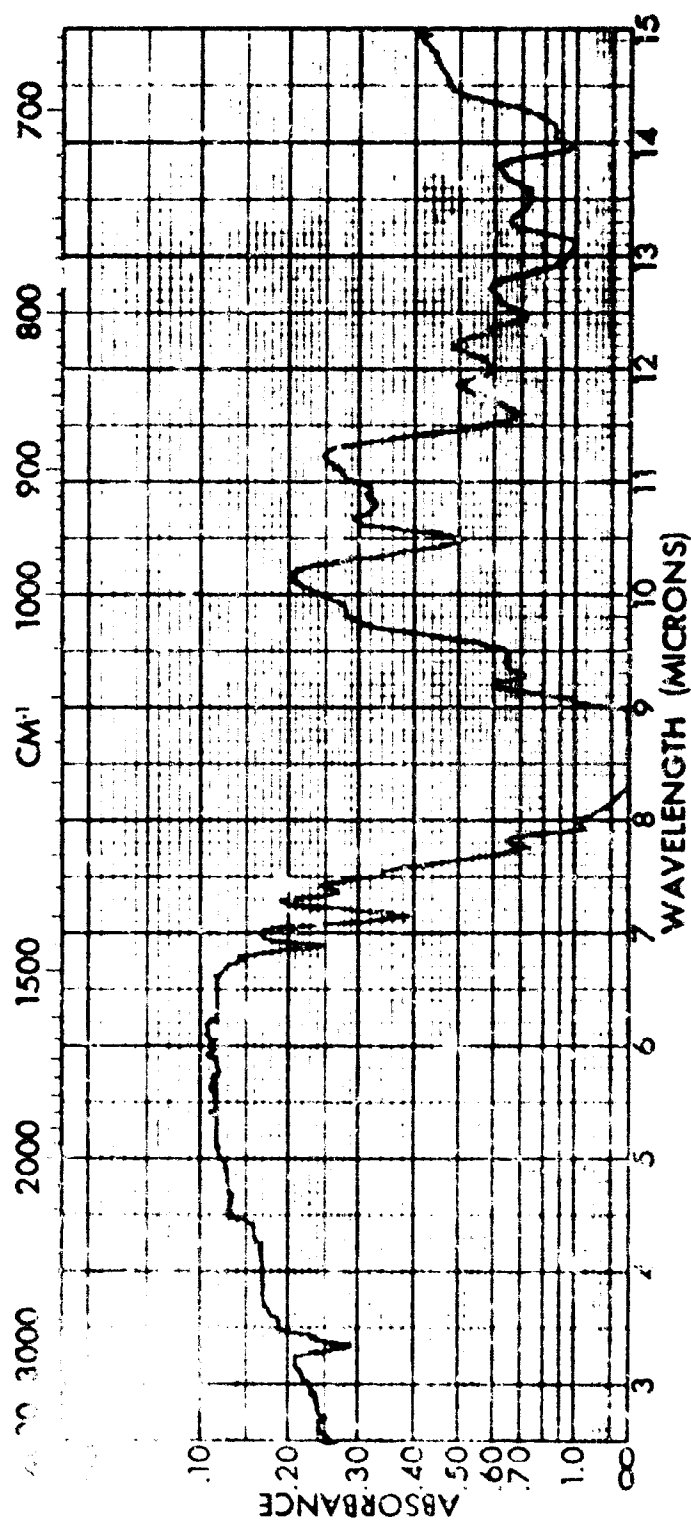


Fig. 10 - Infrared Spectrum of $\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_{4.5}(\text{OC}_2\text{H}_5)_{0.7}$
(Liquid, Thin Film)

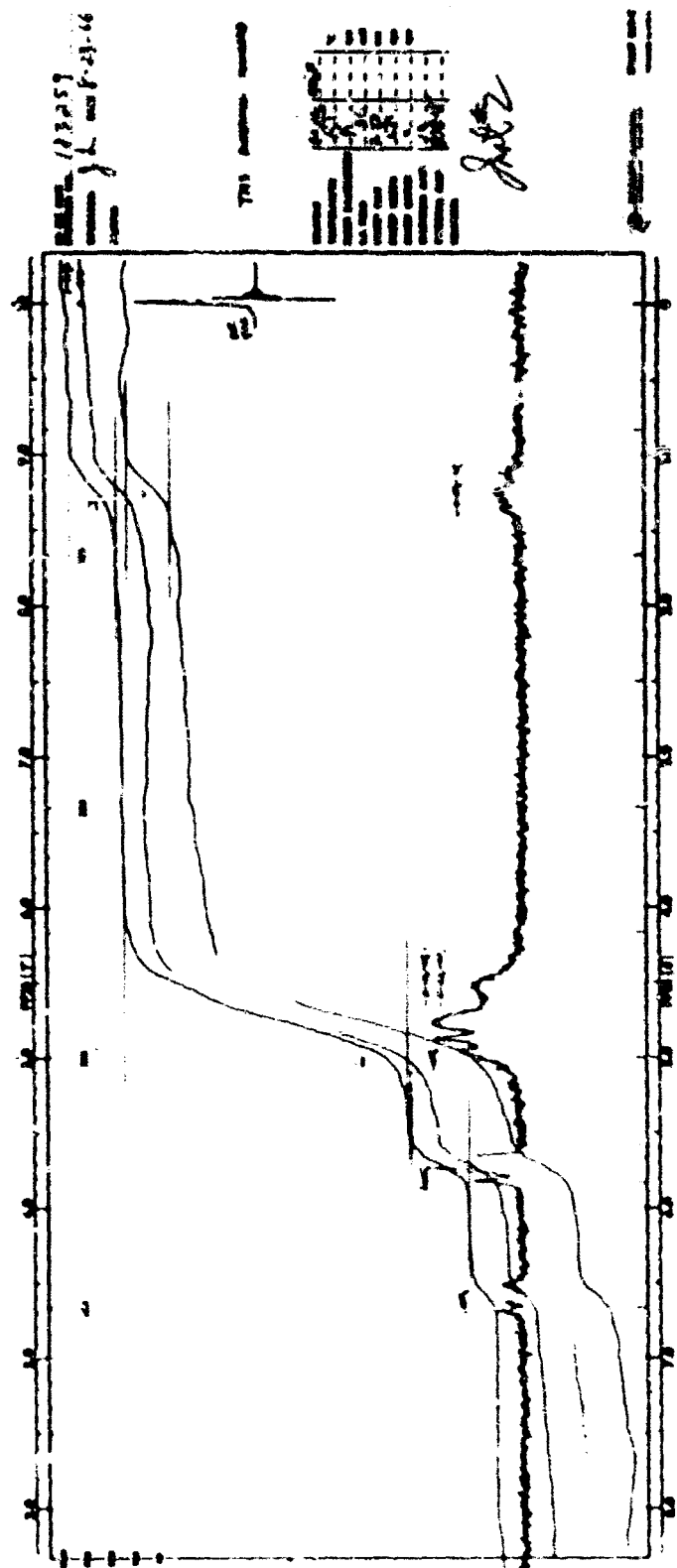


Fig. 11 - Proton Nuclear Magnetic Resonance spectrum of
 $\text{Ta}[\text{OCH}_2(\text{CF}_2)_2\text{CH}_2]_{4.5}(\text{OC}_2\text{H}_5)_{0.7}$

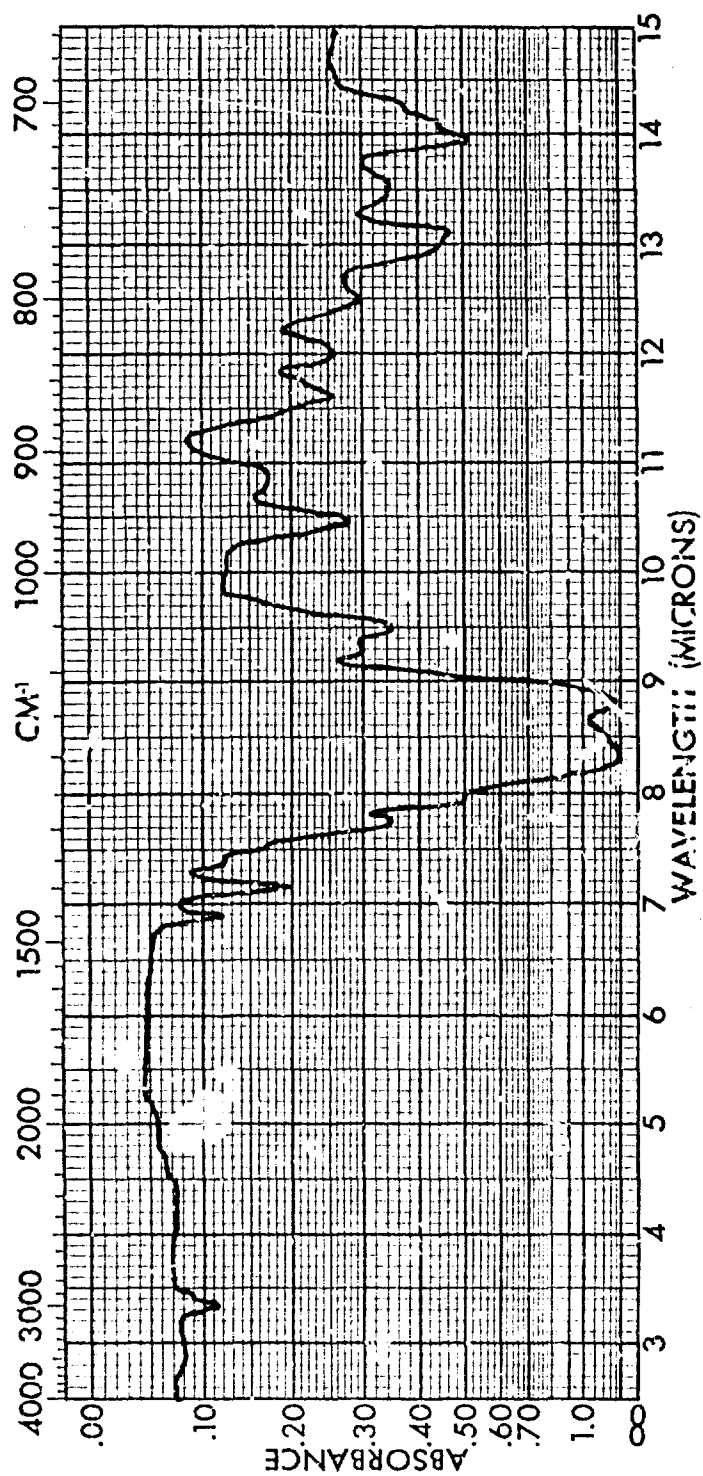


Fig. 12 - Infrared Spectrum of $\text{Ta}[\text{OCH}_2(\text{CF}_2)_5\text{CF}_2\text{H}]_{4.7}(\text{OC}_2\text{H}_5)_{0.3}$

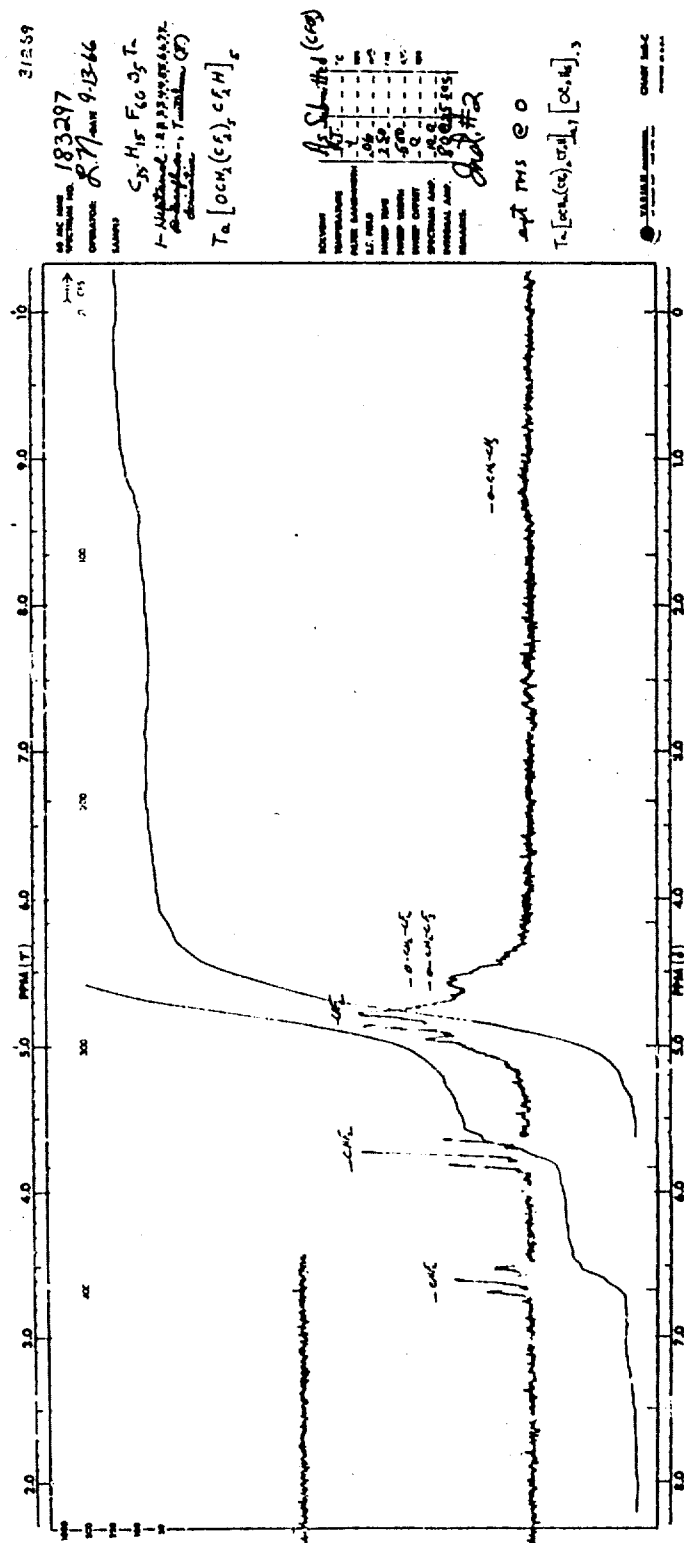


Fig. 13 - Proton Nuclear Magnetic Resonance Spectrum of
Ta[OCH₂(CF₂)₂CF₂H]_{4.7}(OC₂H₅)_{0.3}

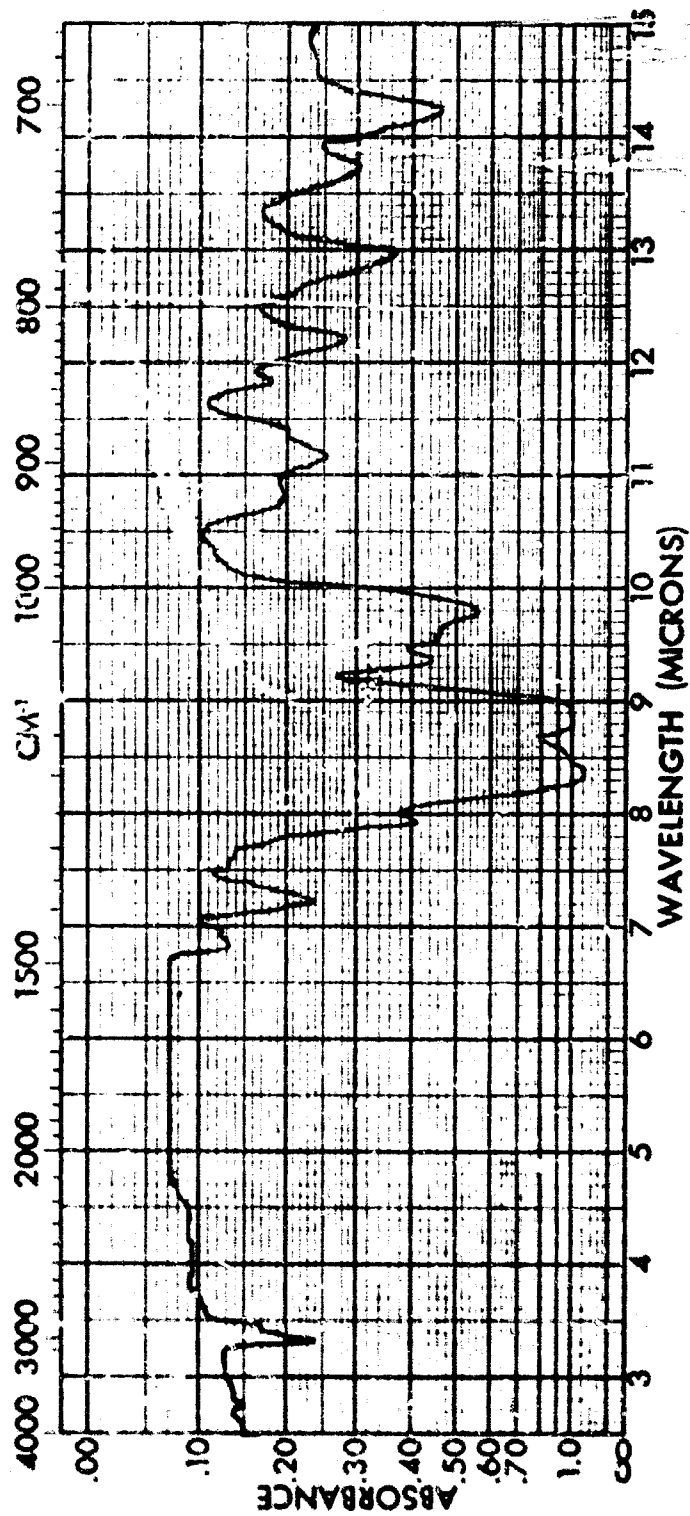


Fig. 14 - Infrared Spectrum of $\text{Ta}[\text{OC}(\text{CH}_3)_2(\text{CF}_2)_5\text{CF}_2\text{H}]_5[\text{OC}_2\text{H}_5]_4$
(Liquid, Thin Film)

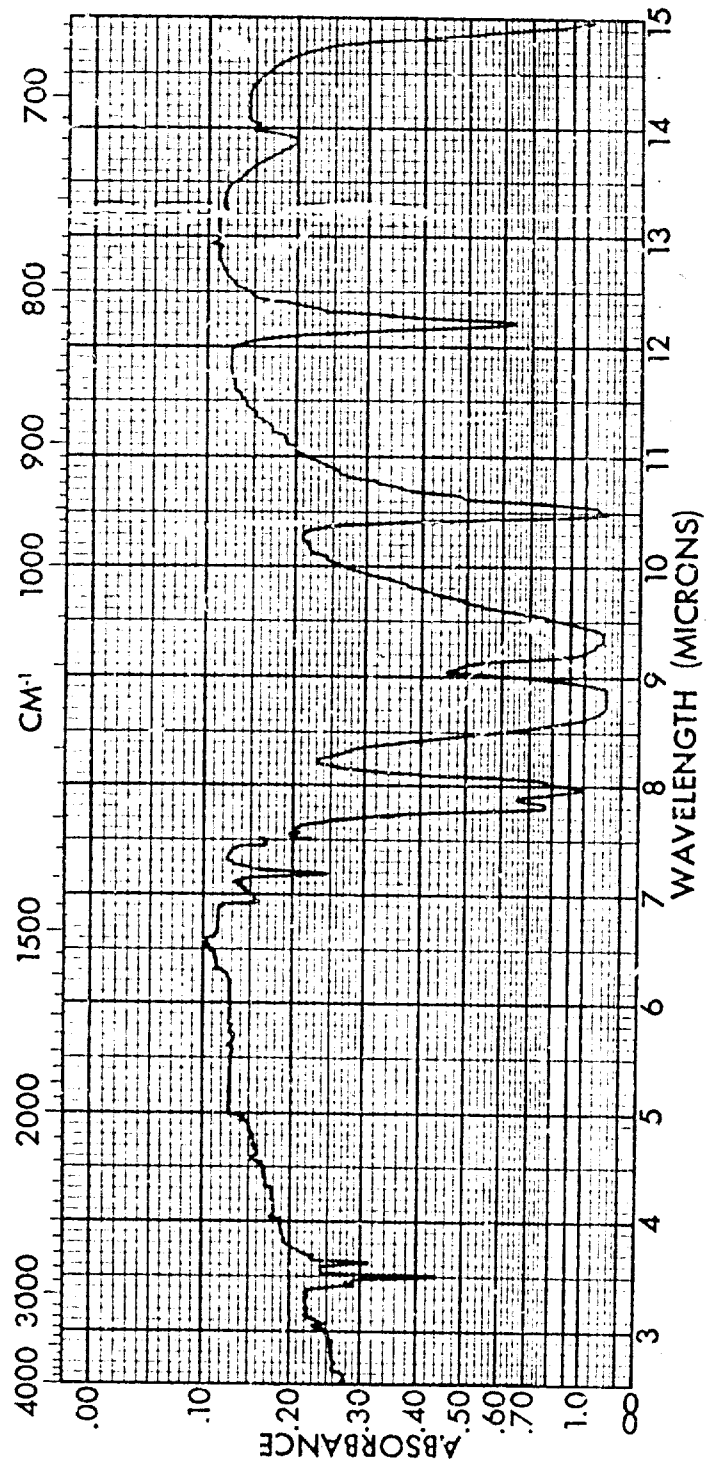


Fig. 16 - Infrared Spectrum of Thallium Trifluoroethoxide
(Solid, Split Mull)

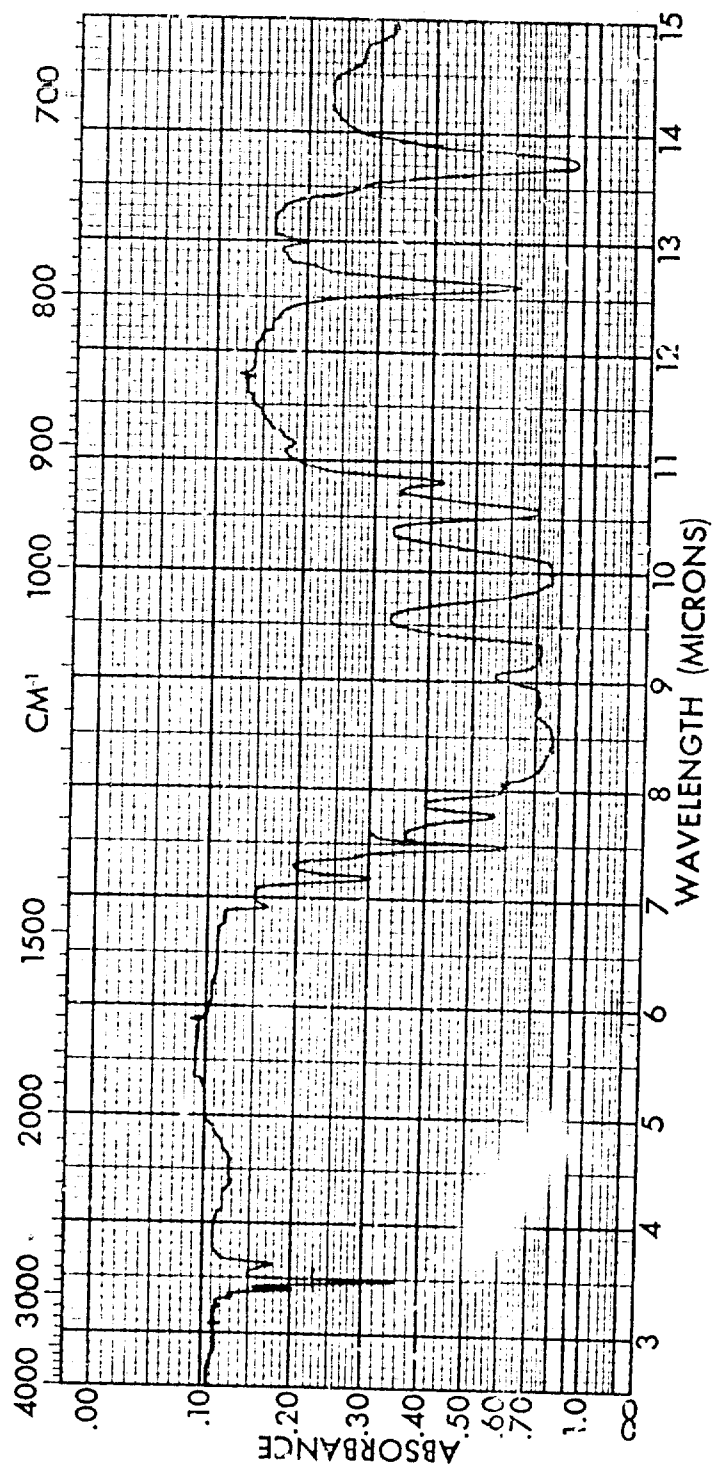


Fig. 17 - Infrared Spectrum at Thallium Pentafluoropropoxide
(Solid, Split Mull)

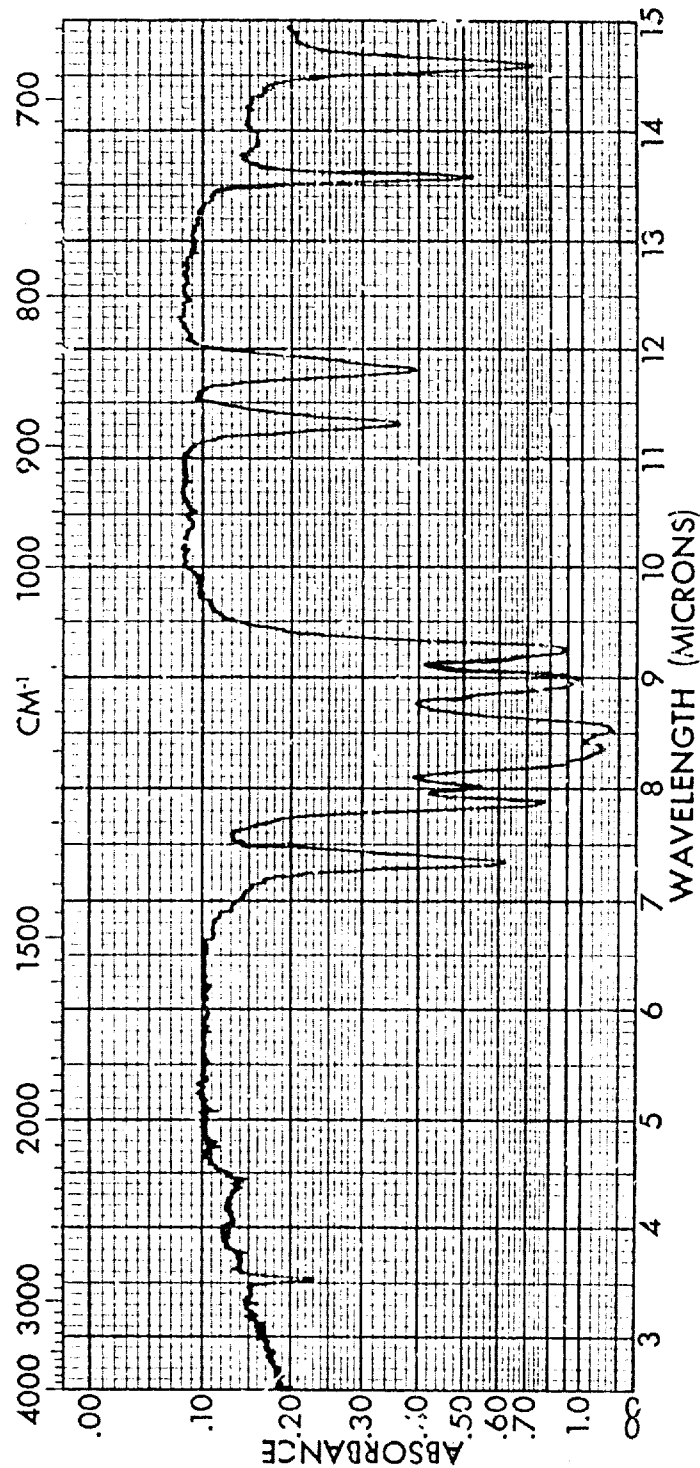


Fig. 18 - Infrared Spectrum of Thallium Hexafluoroisopropoxide
(Solid, Split Cell)

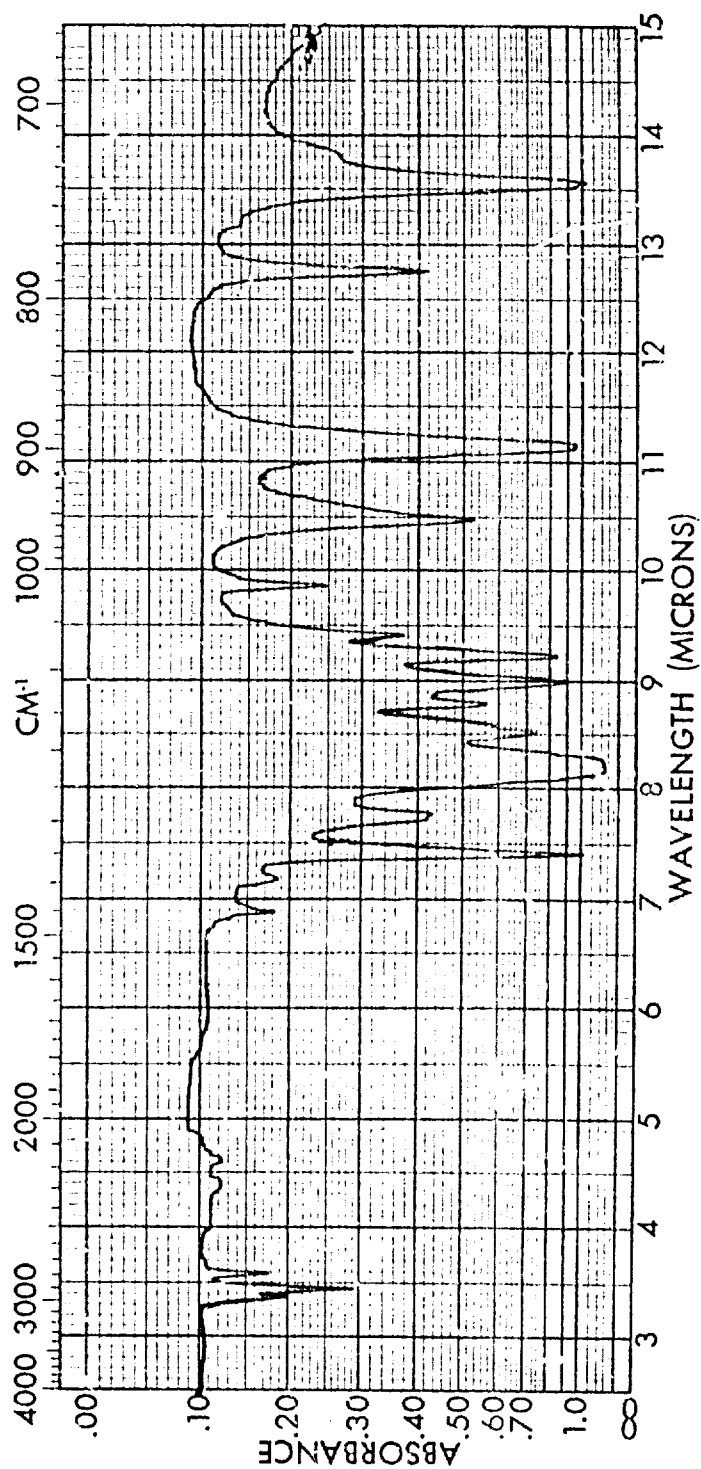


Fig. 19 - Infrared Spectrum of Thallium Heptafluorobutoxide
(Solid, Split Mull)

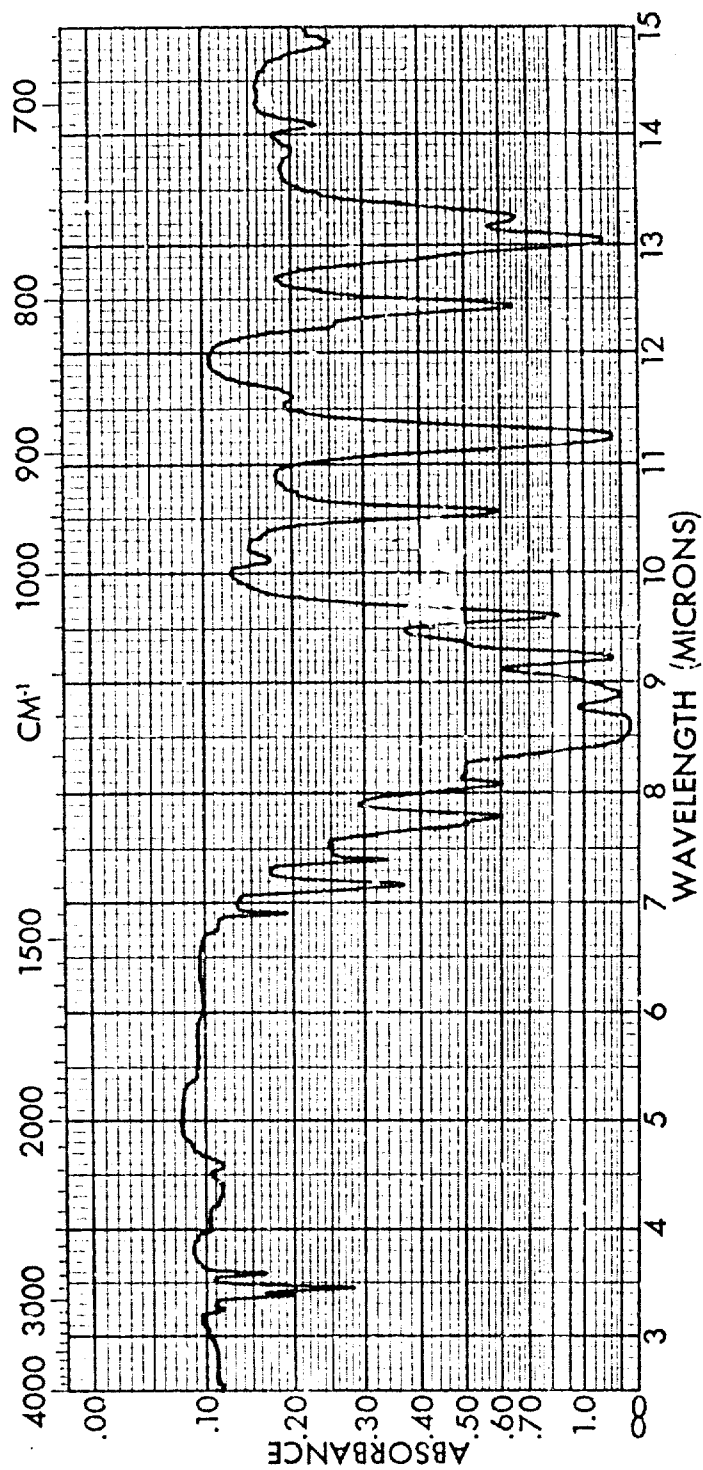


Fig. 20 - Infrared Spectrum of Thallium Octafluoropentoxide
(Solid, Split Malt)

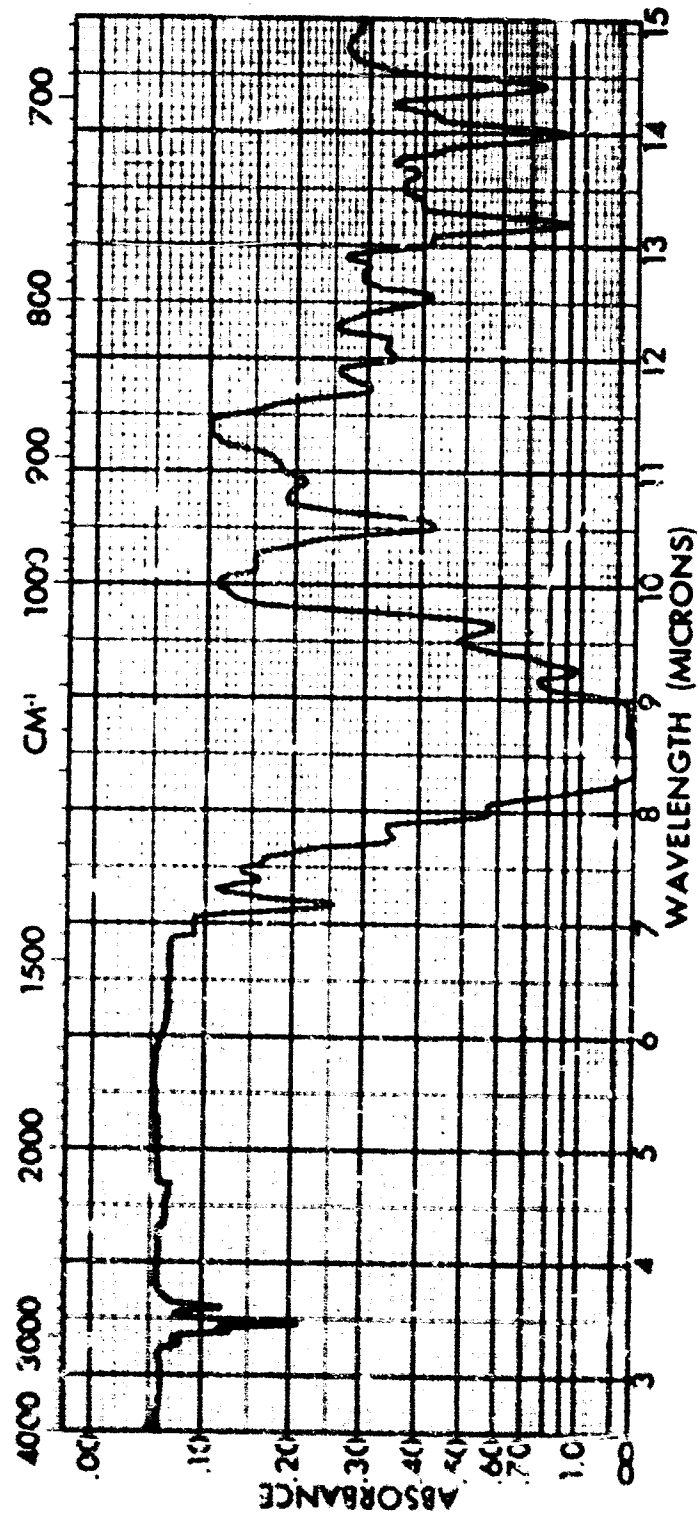


Fig. 21 - Infrared Spectrum of Thallium Dodecafluoroheptoxide
(Liquid, Thin Film)

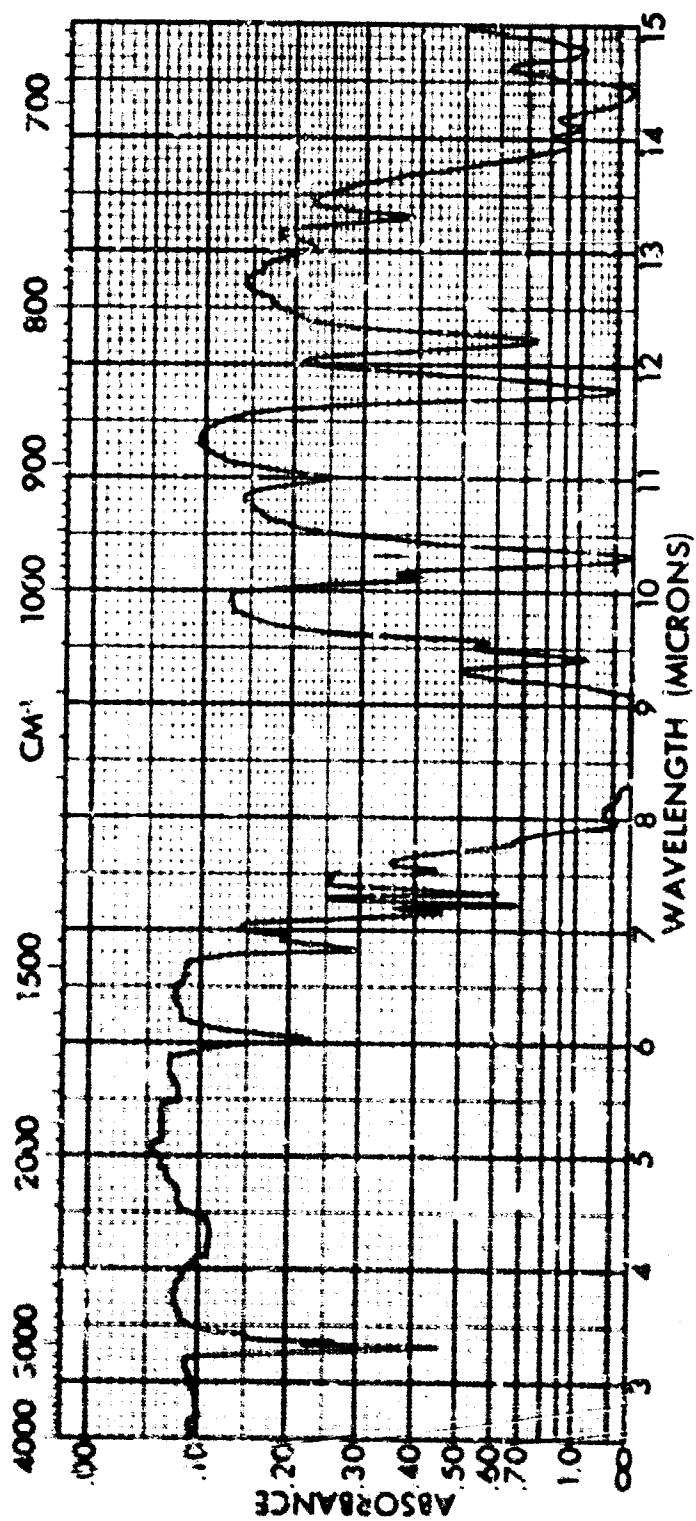


Fig. 22 - Infrared Spectrum of Thallium Dodecafluoro-2-methyl-2-octoxide (Solid, Spill Mull)

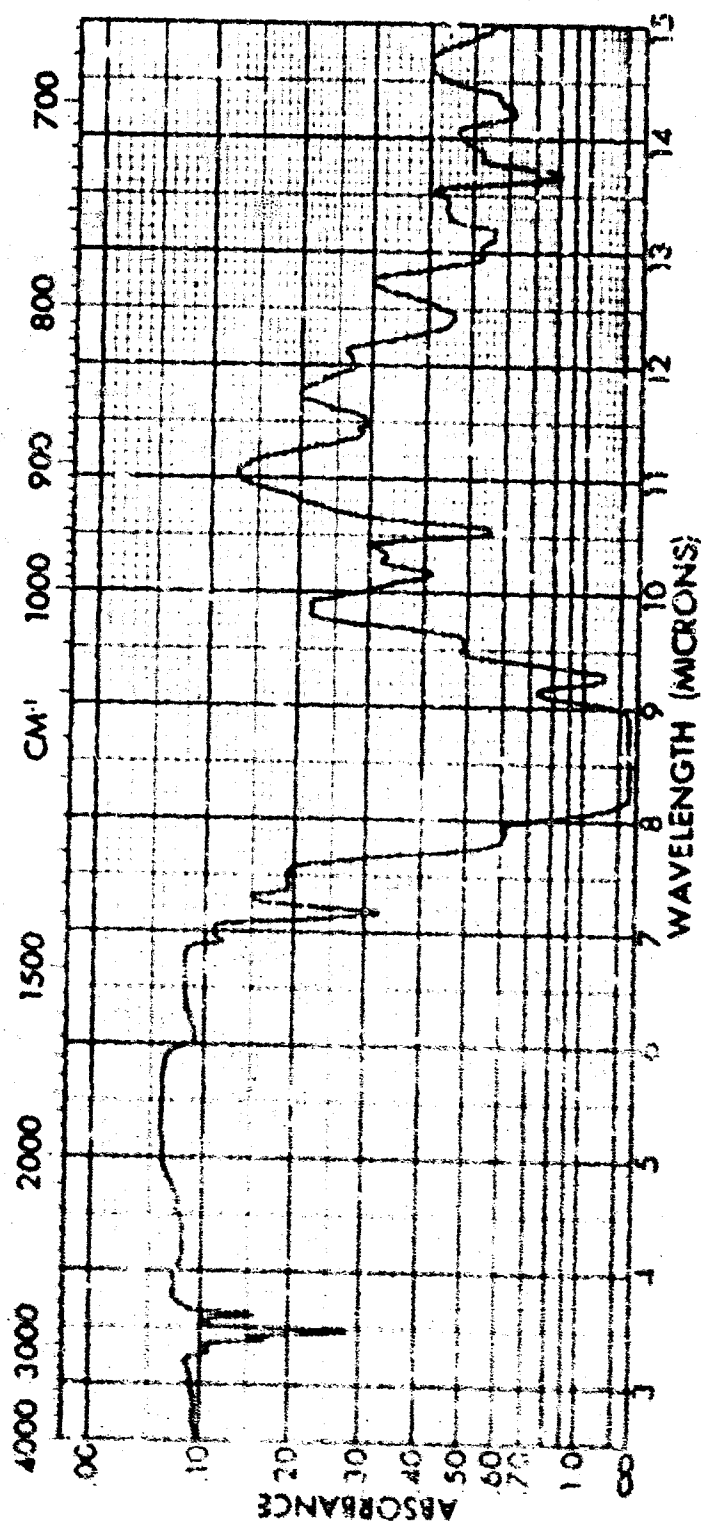


Fig. 25 - Infrared Spectrum of Thallium Hexadecafluorooxide
(Liquor, thin film)

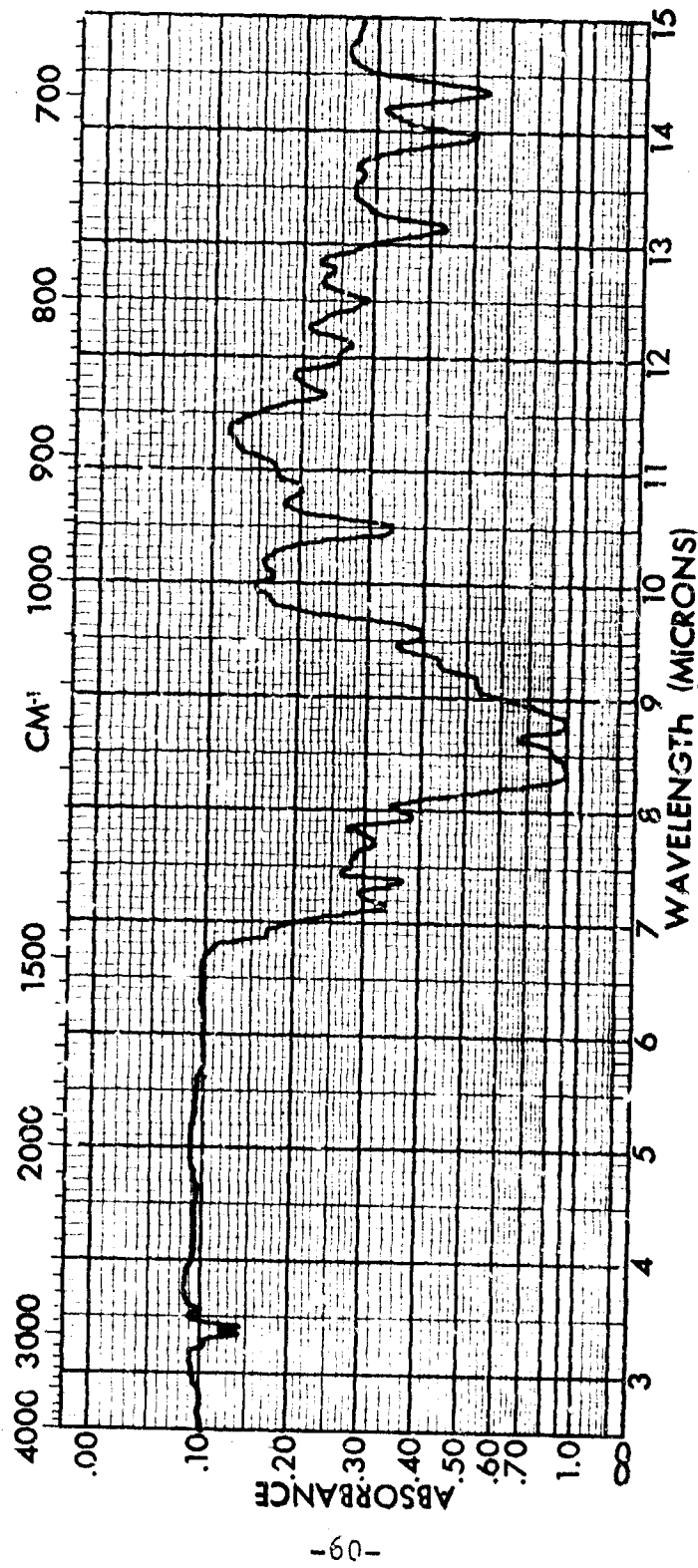


Fig. 24 - Infrared Spectrum of Lead Dodecafluorooheptoxide
(Solid, Split Mull)

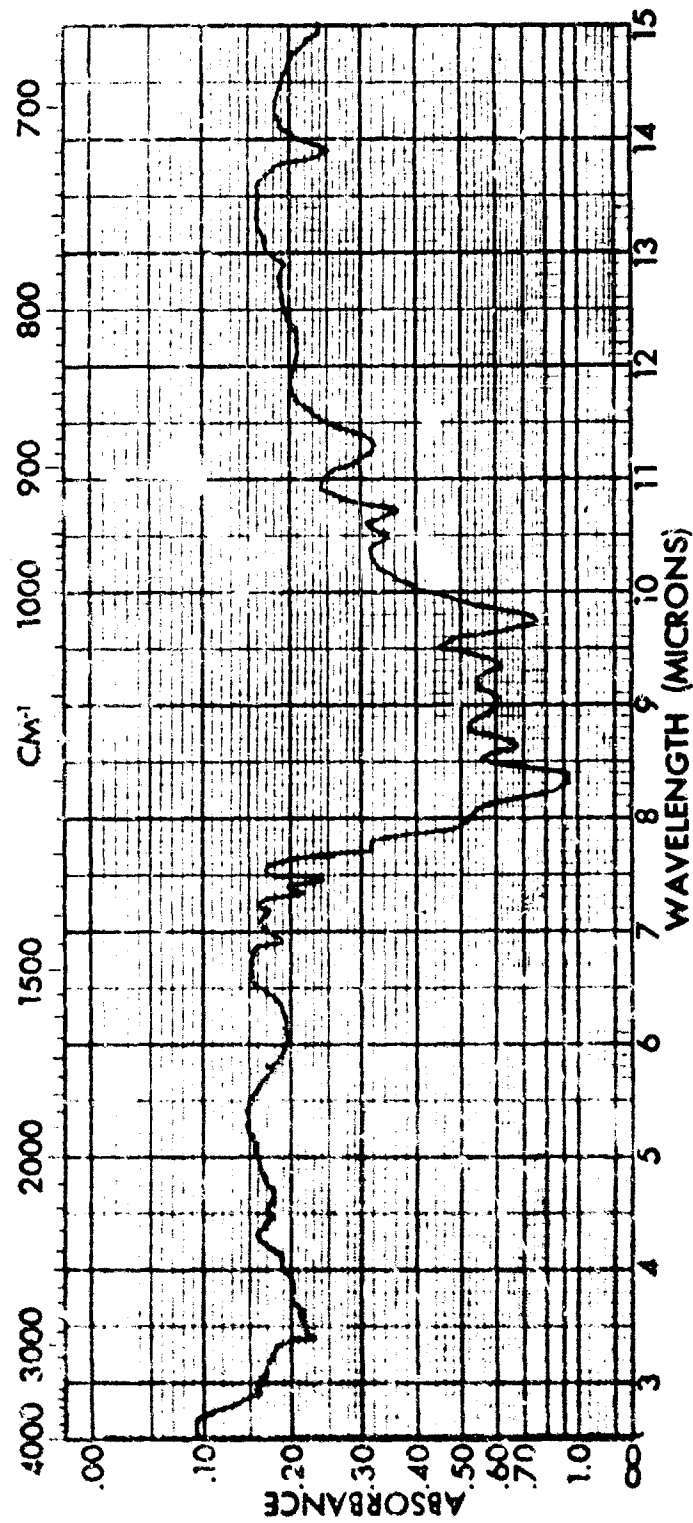


Fig. 25 - Infrared Spectrum of bis(Pentafluoropropyl) Hydrogen Phosphate (Liquid, Thin Film)

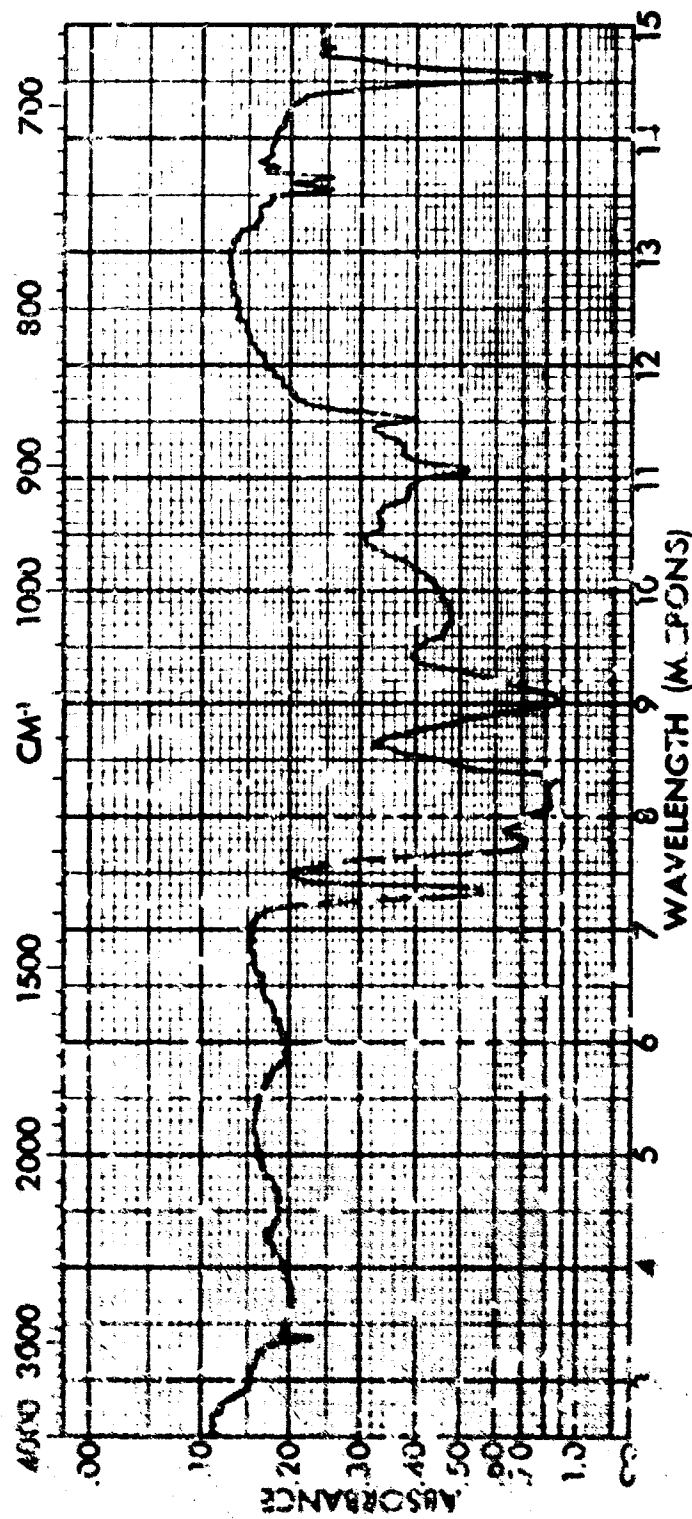


Fig. 26 - Infrared Spectrum of bis(Hexafluoroisopropyl) Hydrogen Phosphate (Solid, Thin Film)

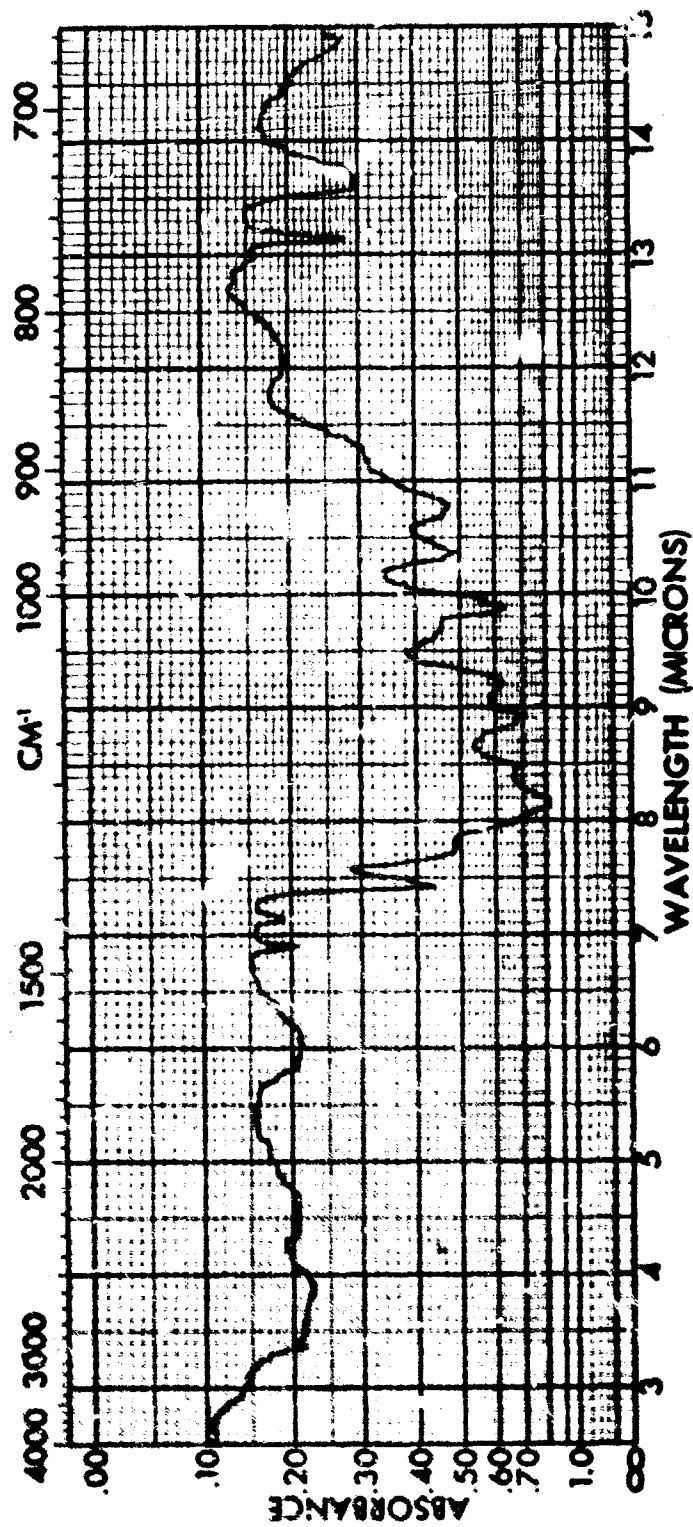


Fig. 27 - Infrared Spectrum of bis(Heptafluorobutyl) Hydrogen Phosphate (Solid, Thin Film)

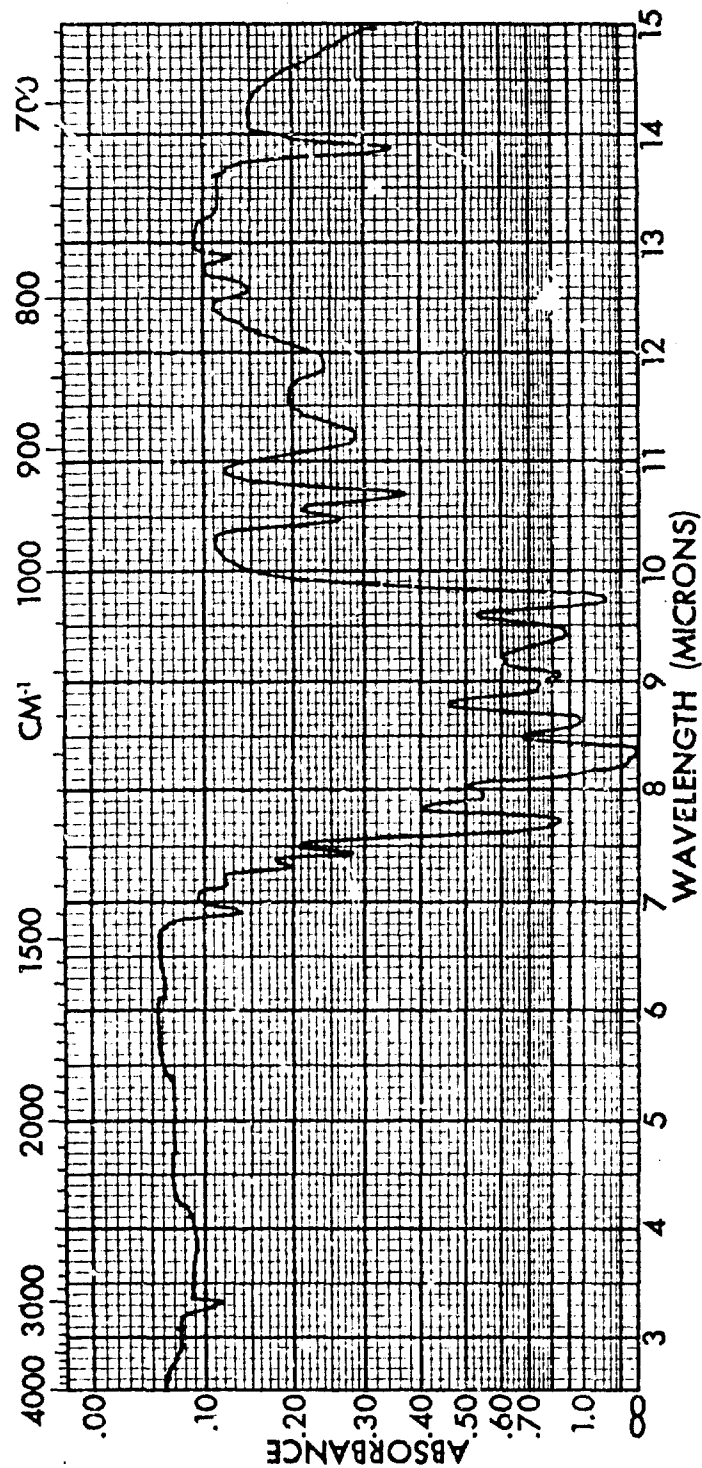


Fig 28 - Infrared Spectrum of bis(Pentafluoropropyl)
Chlorophosphate (Liquid, Thin Film)

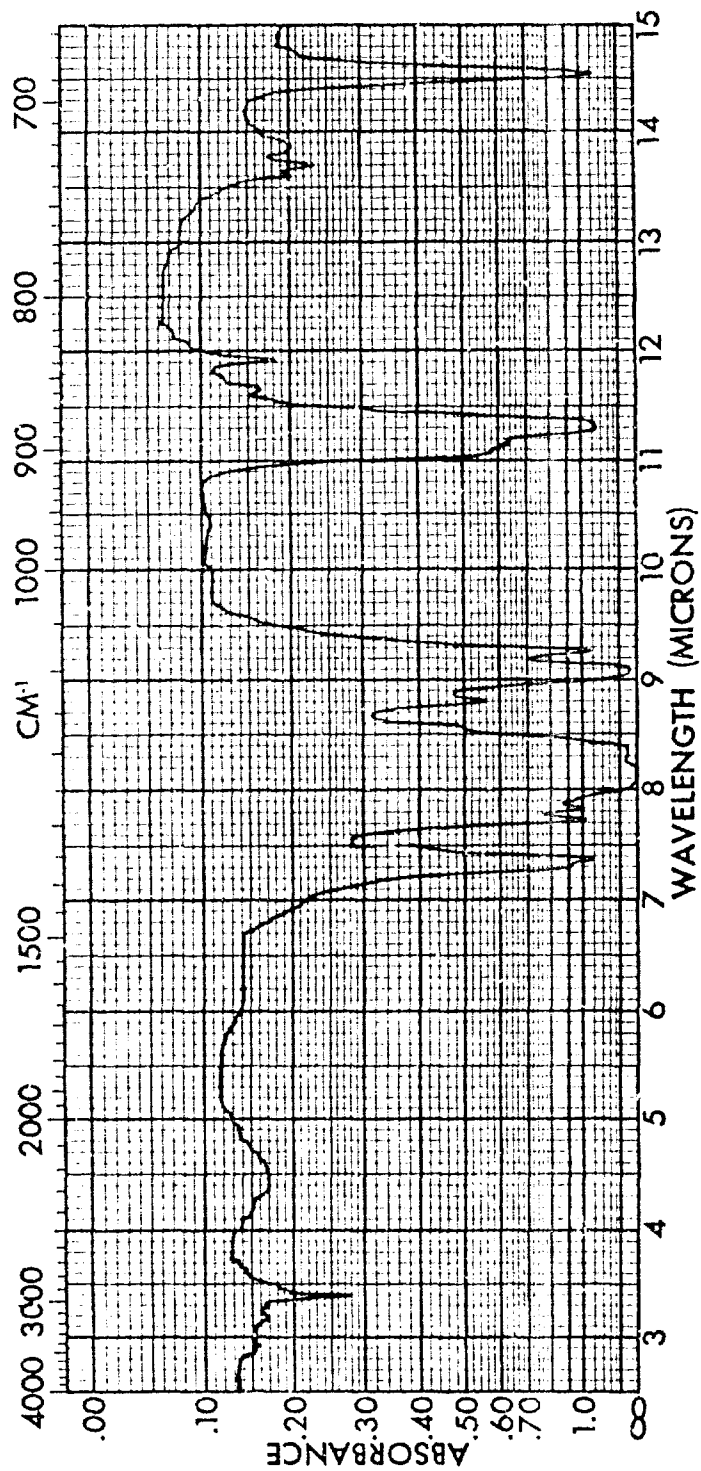


Fig. 29 - Infrared Spectrum of Thallium bis(Hexafluoroisopropyl) Phosphate
(Solid, Split Mull)

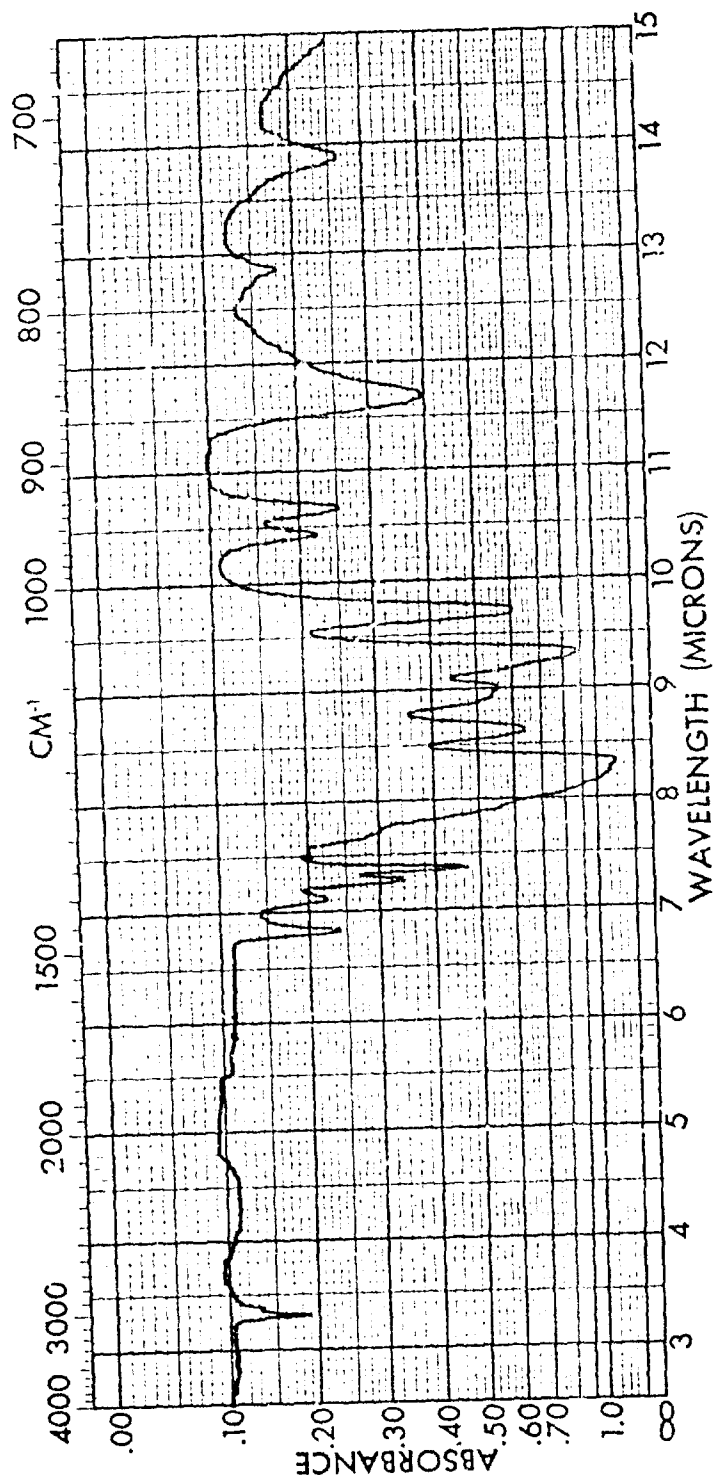


Fig. 30 - Infrared Spectrum of Thallium bis(Pentafluoropropyl) Phosphate
(Solid, Split Mull)

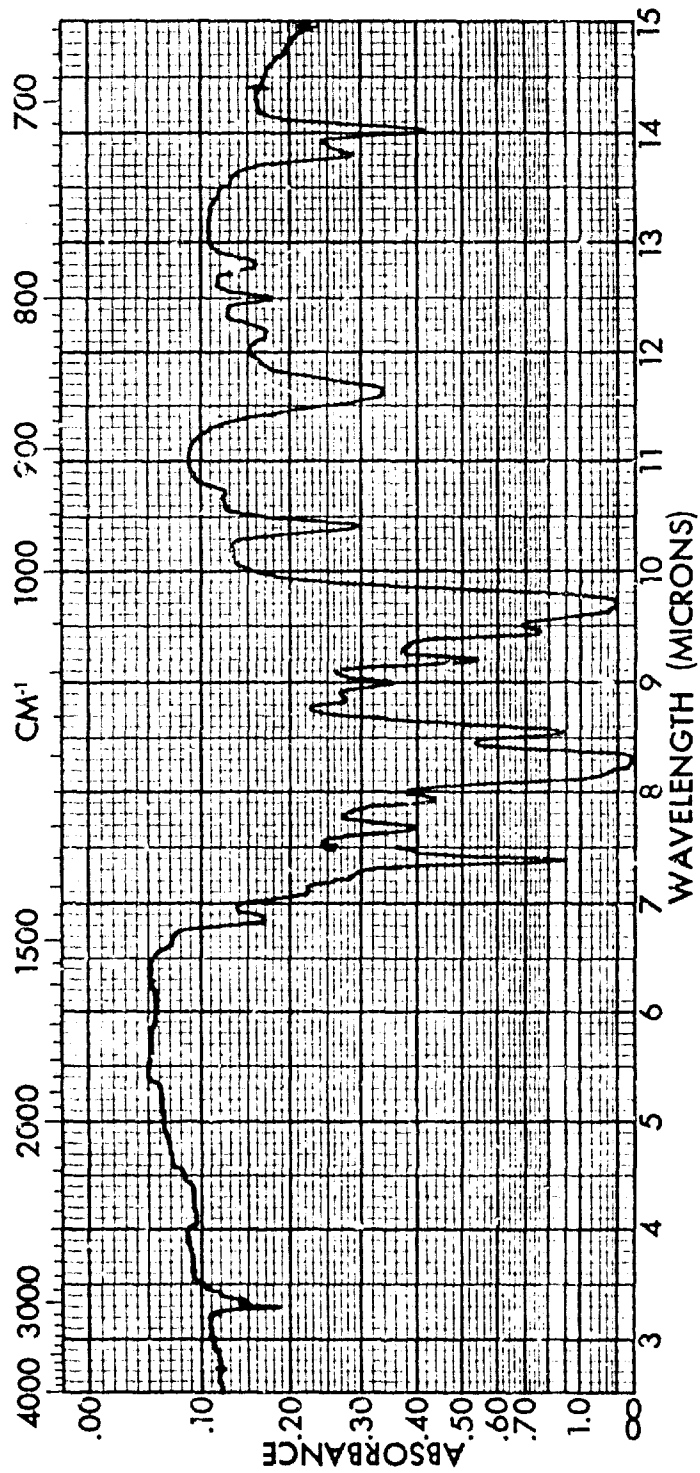


Fig. 31 - Infrared Spectrum of Lead bis(Pentafluoropropyl) Phosphate
(Solid, Split Mull)

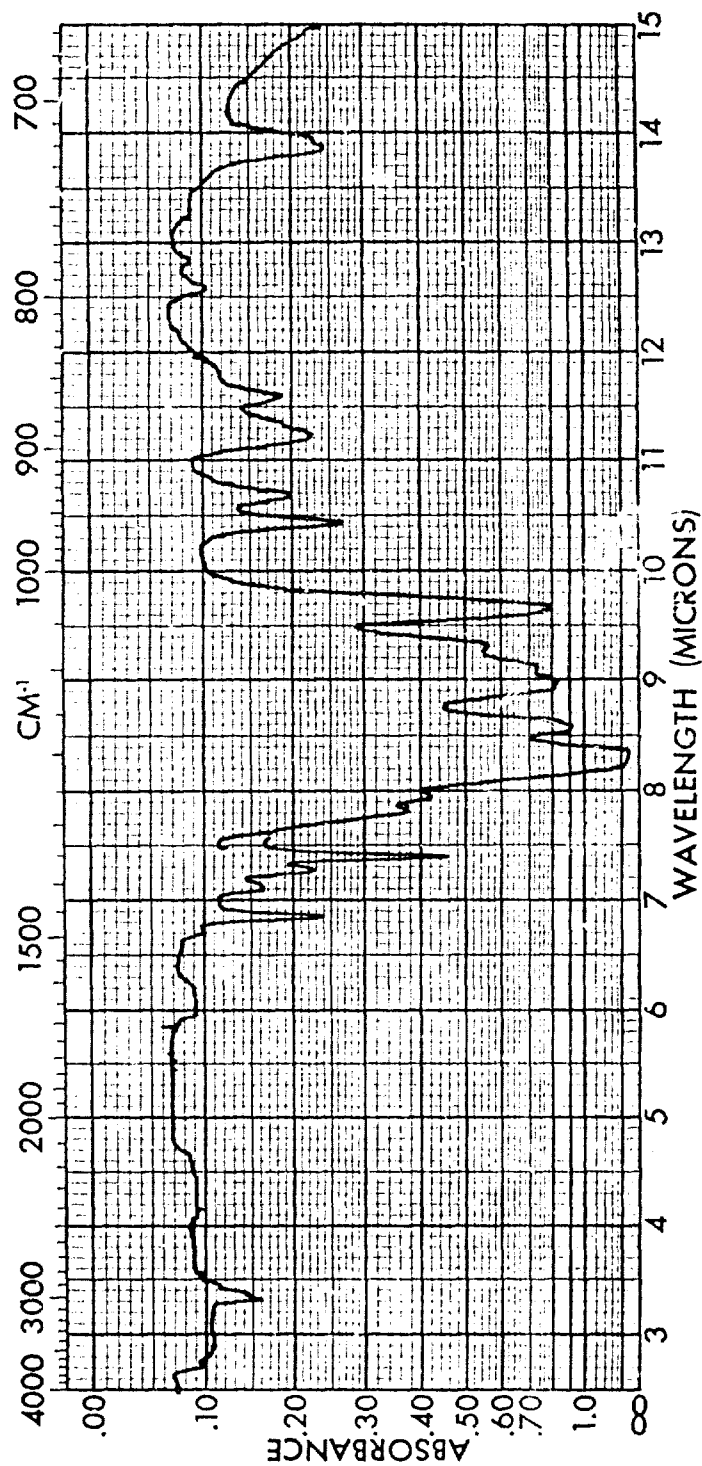


Fig. 32 - Infrared Spectrum of Thorium bis(Pentafluoropropyl) Phosphate
(Solid, Split Mull)

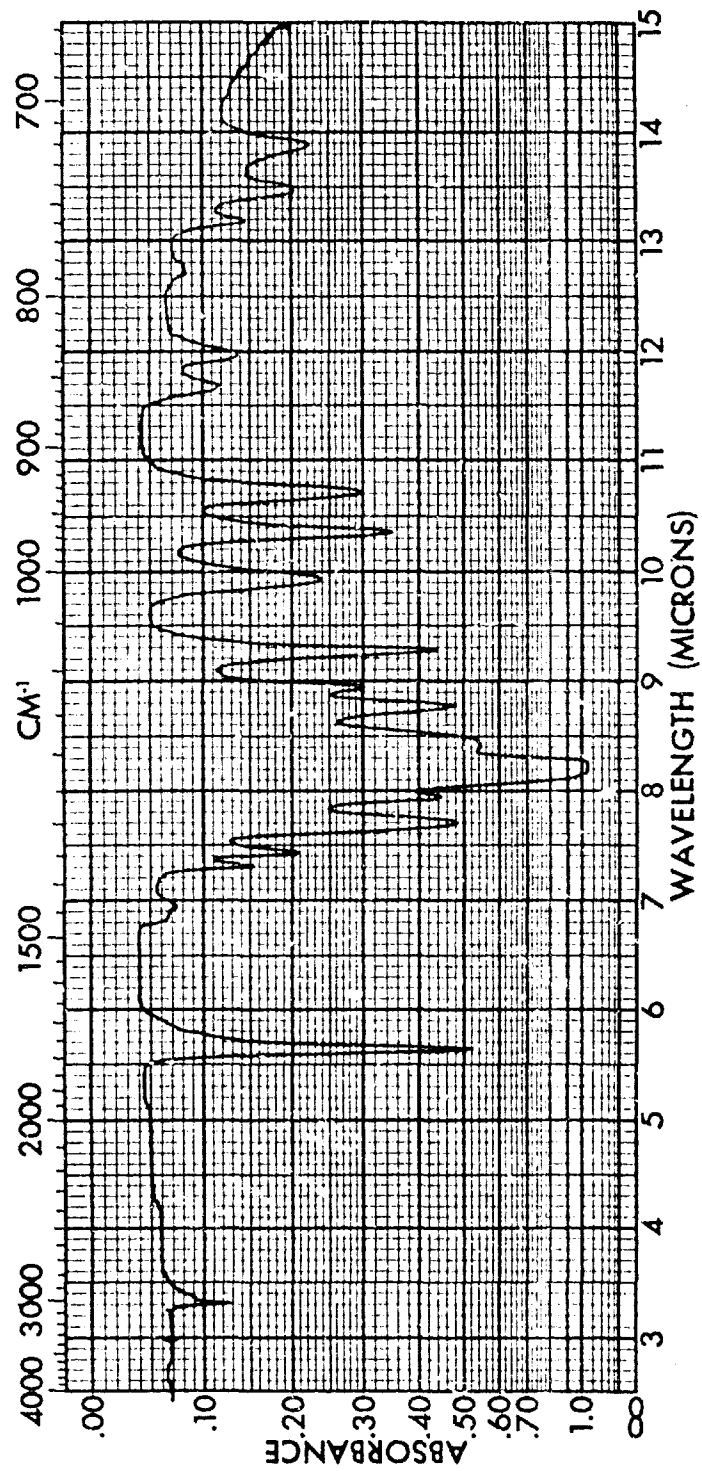


Fig. 33 - Infrared Spectrum of Ethyl Heptafluorobutyrate
(Liquid, Thin Film)

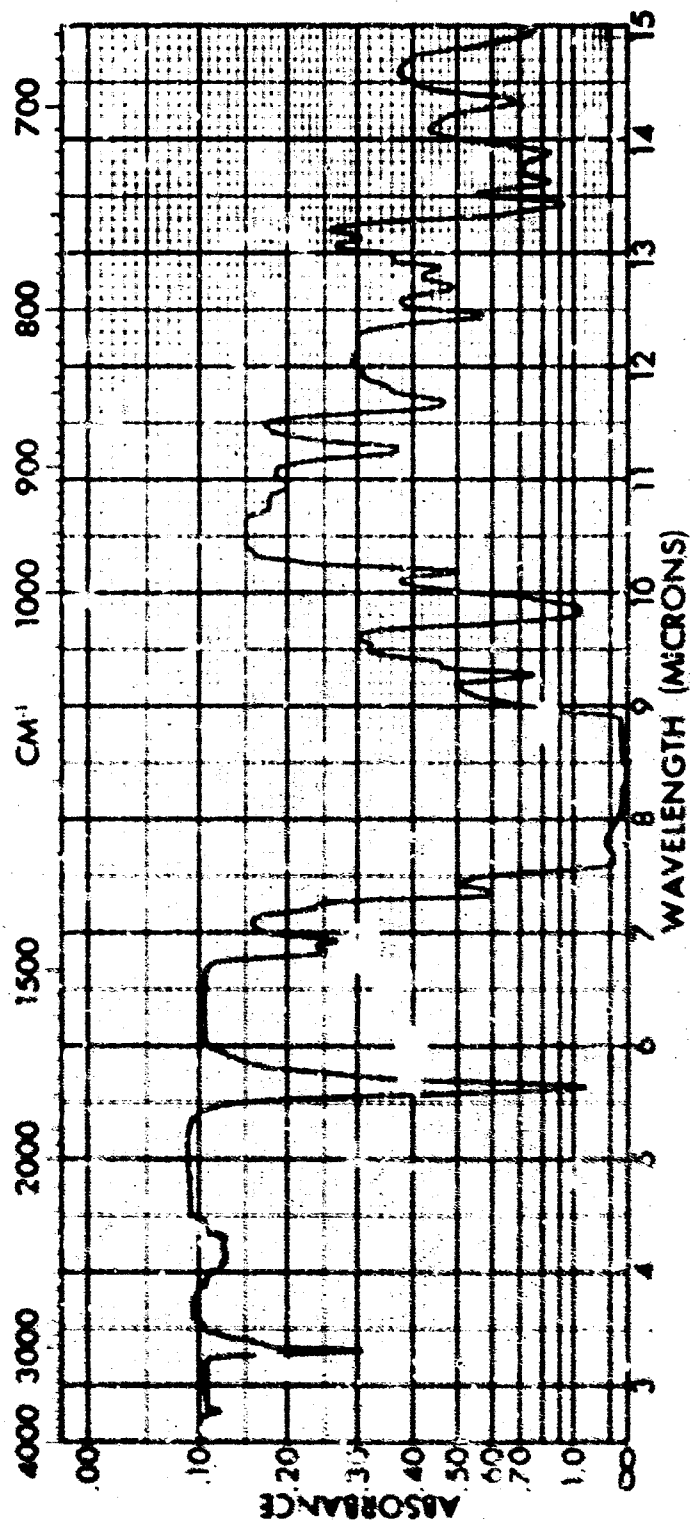


Fig. 24 - Infrared Spectrum of Ethyl Pentadecafluorooctanoate (Liquid, Thin Film)

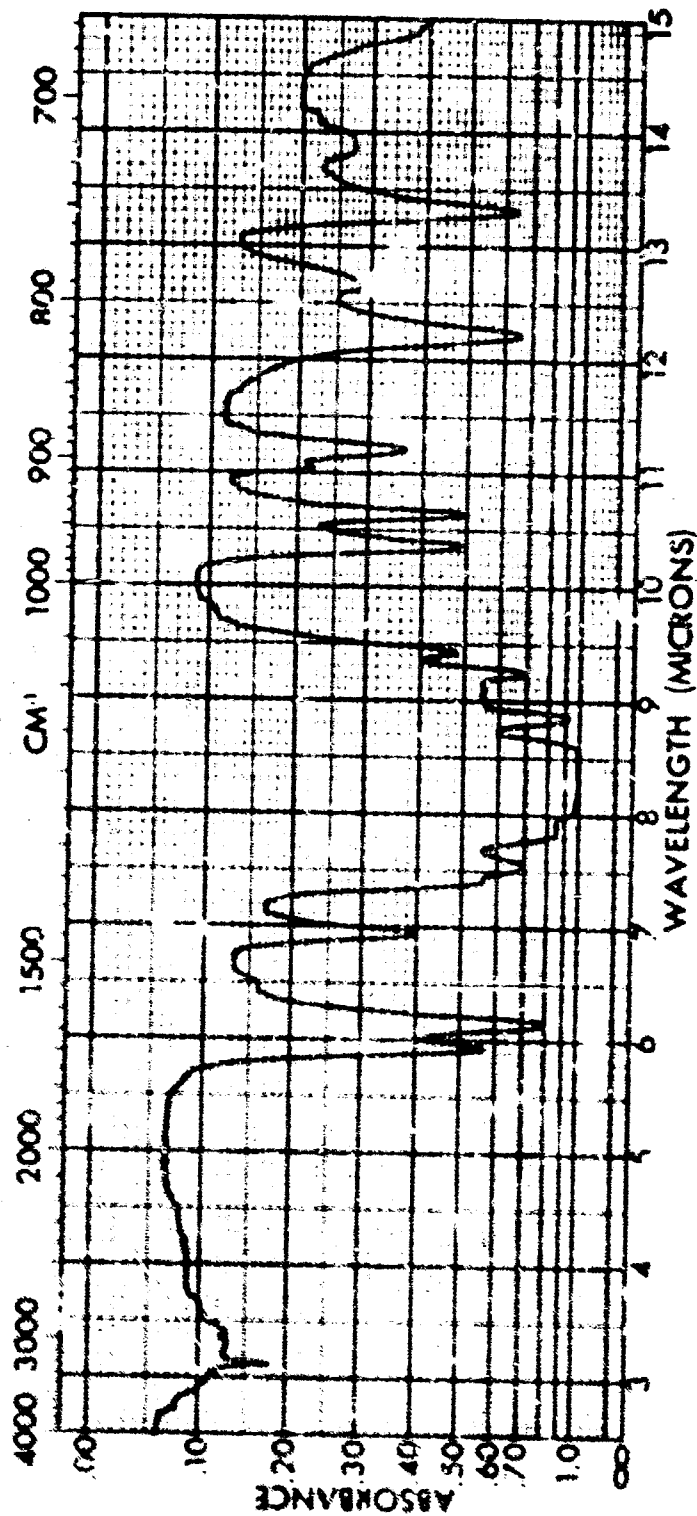


Fig. 10 - Infrared Spectrum of Decafluoro-2,4-heptanedione
(Liquid, Thin Film)

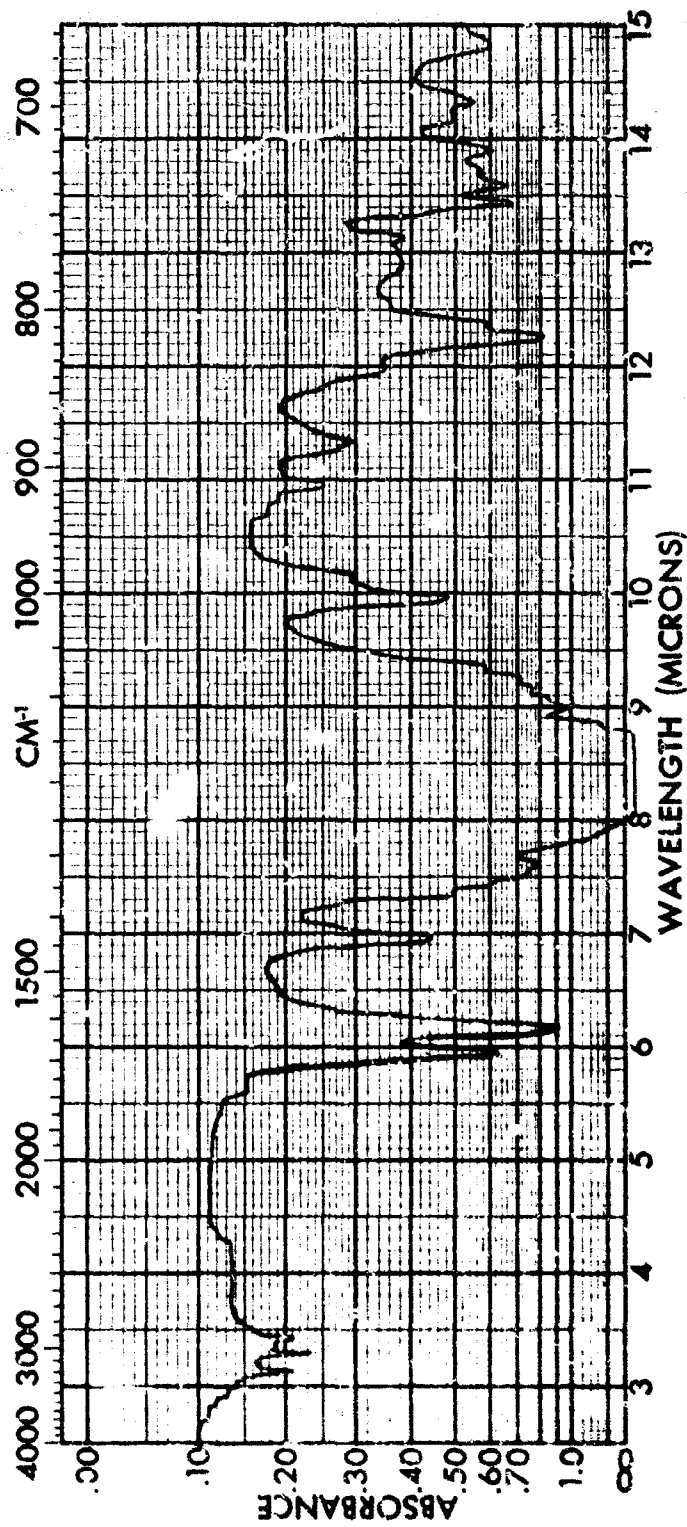


Fig. 36 - Infrared Spectrum of Octadecafluoro-2,4-undecanedione (Liquid, Thin Film)

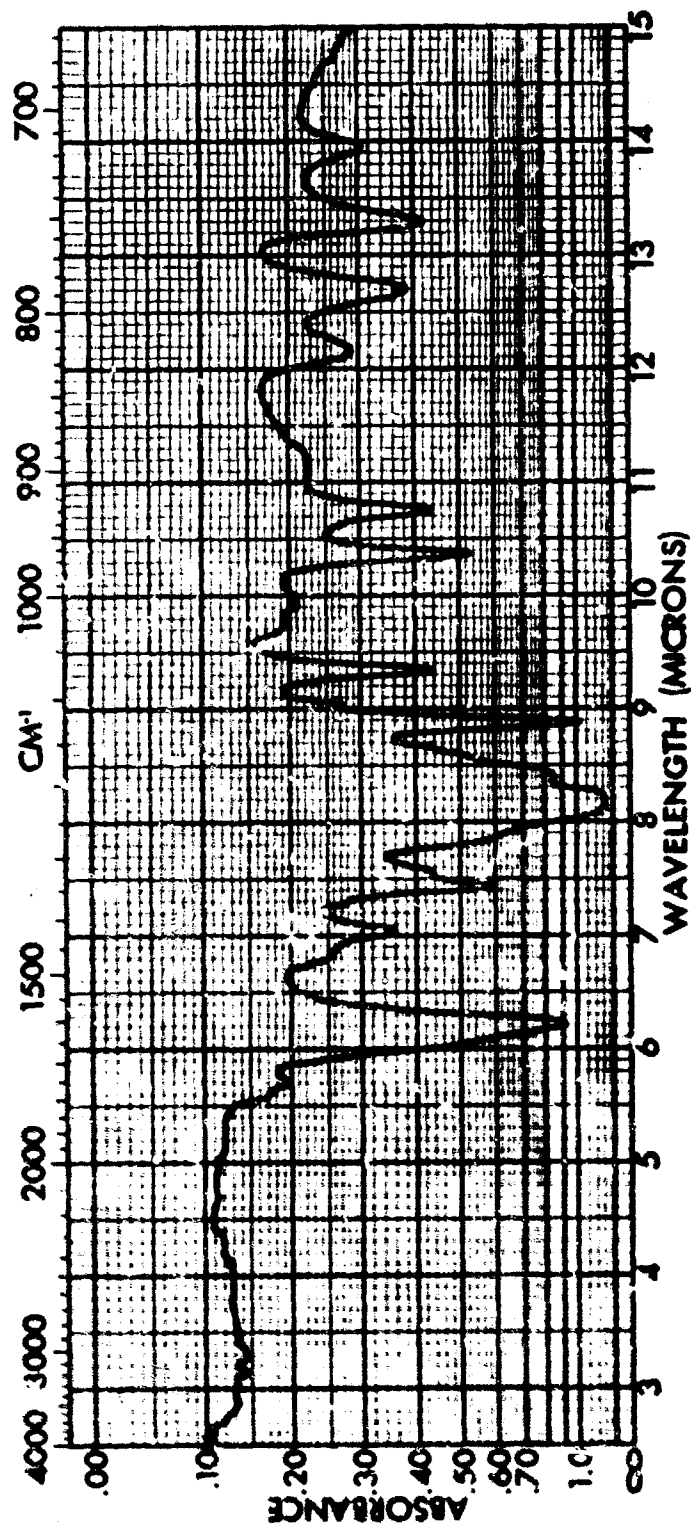


Fig. 37 - Infrared Spectrum of Heptafluoro-2,4-heptanedione
(Liquid, Thin Film)

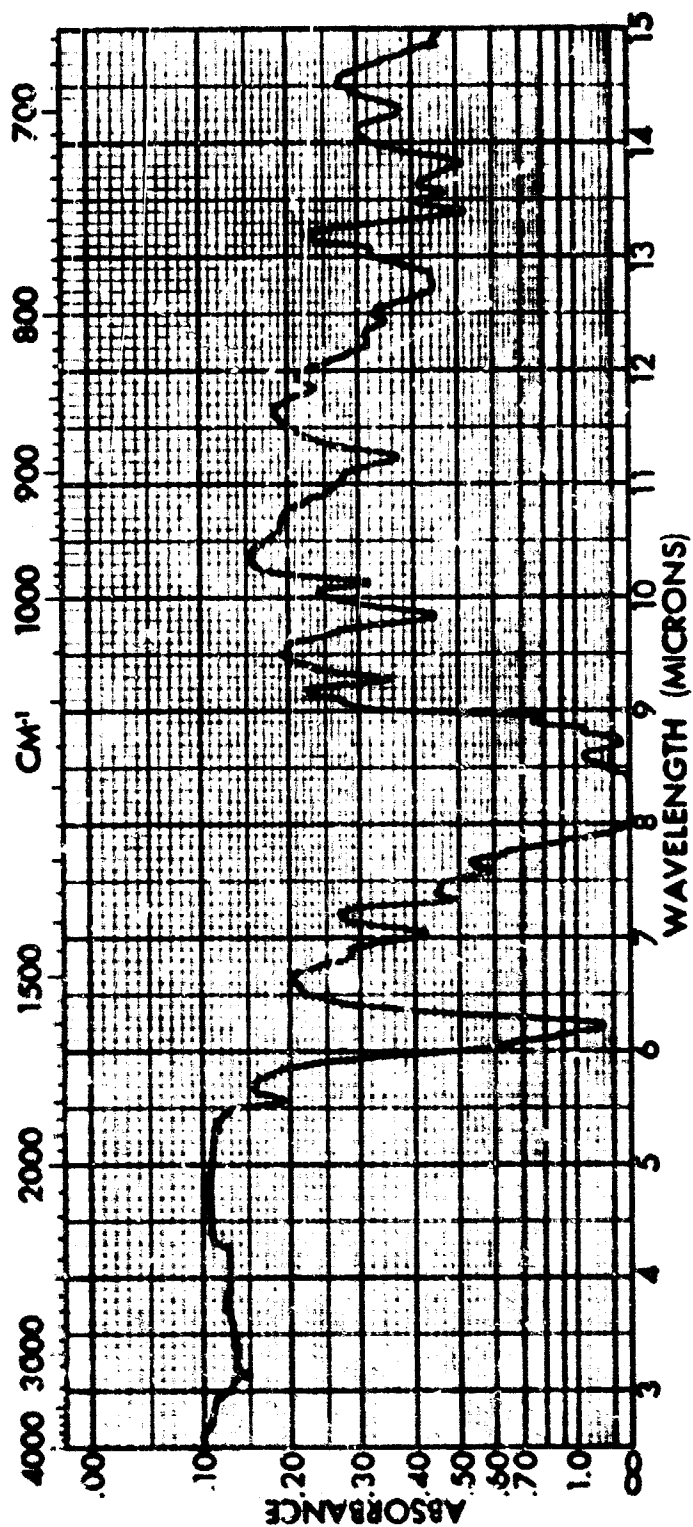


Fig. 38 - Infrared Spectrum of Pentadecafluoro-2,4-undecanedione
(Liquid, Thin Film)

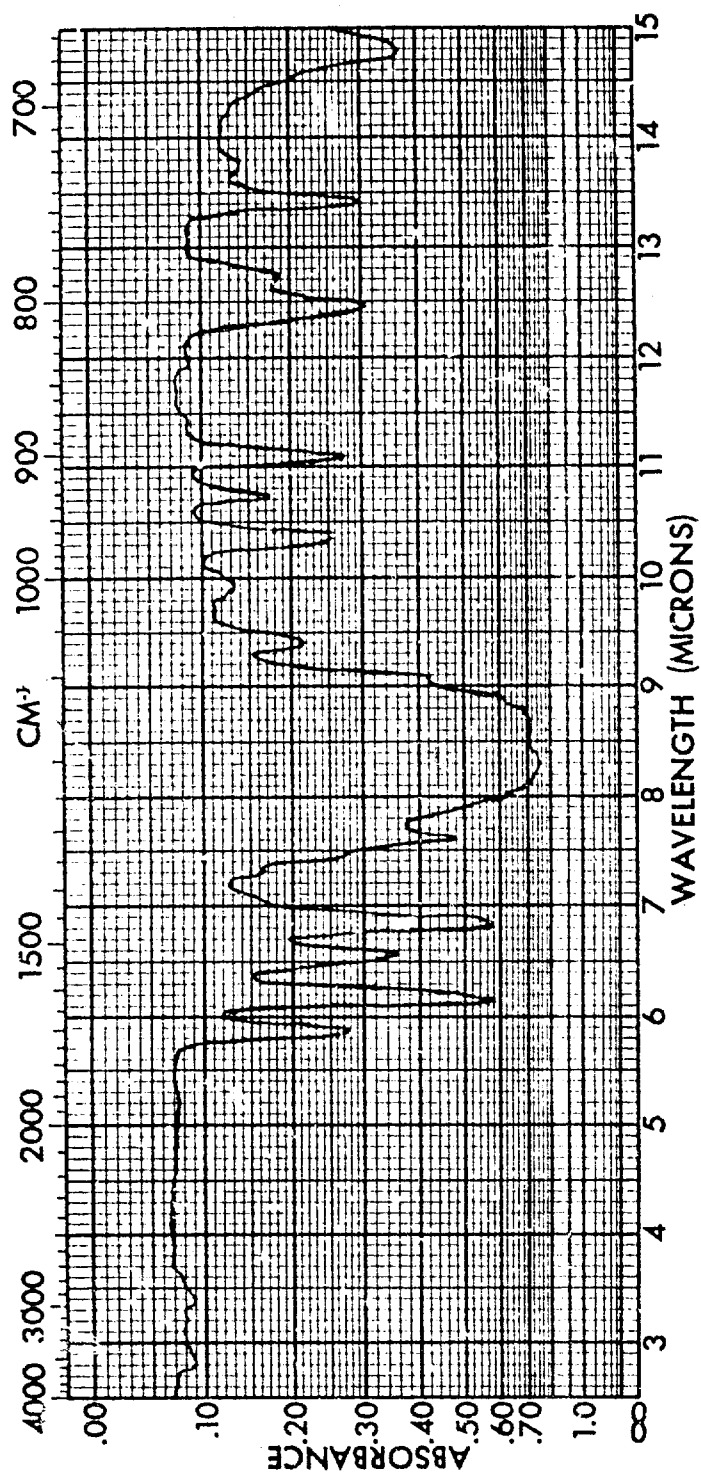


Fig. 39 - Infrared Spectrum of Copper bis(Decafluoro-2,4-heptanedionate)
(Liquid, Thin Film)

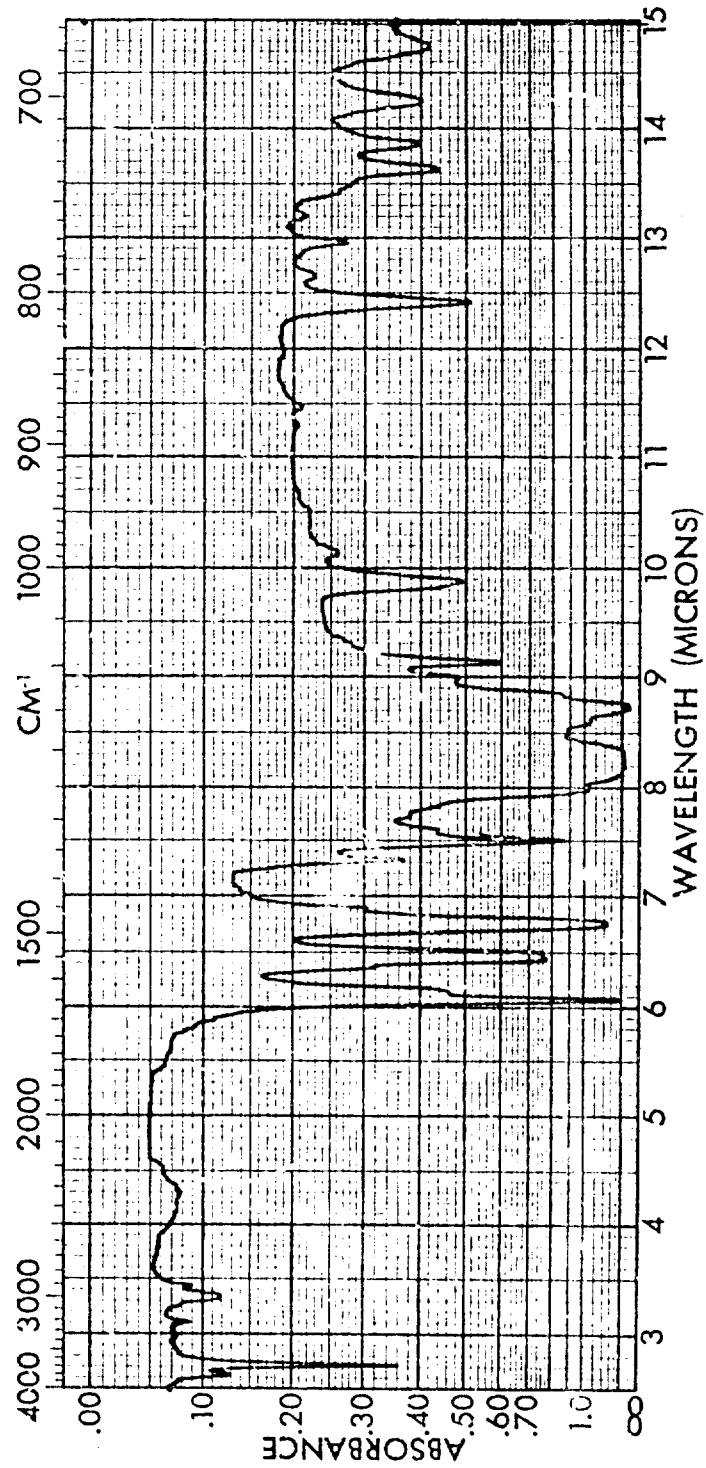


Fig. 40 - Infrared Spectrum of Copper bis(Octadecafluoro-2,4-undecanedionate) Monohydrate (Solid, Split Mull)

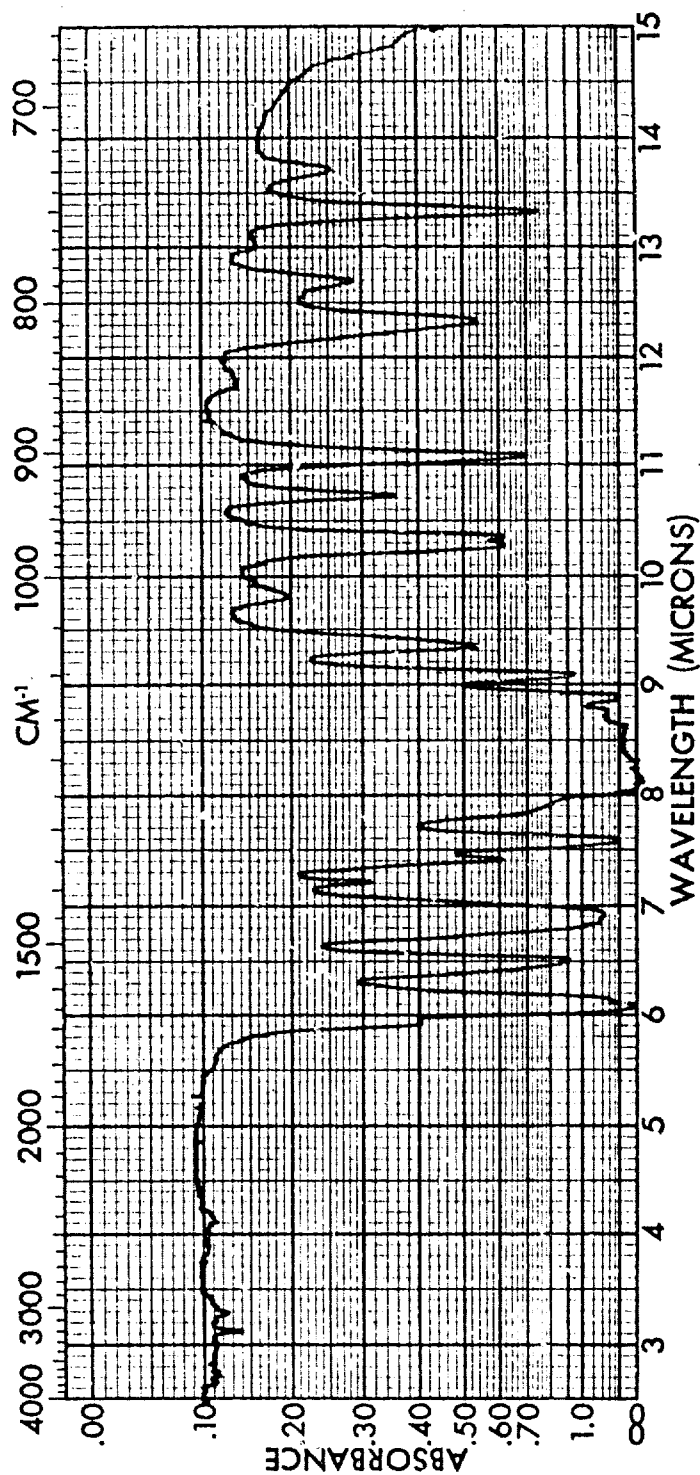


Fig. 41 - Infrared Spectrum of Thorium tetrakis
(Decafluoro-2,4-heptanedionate) (Liquid, Thin Film)

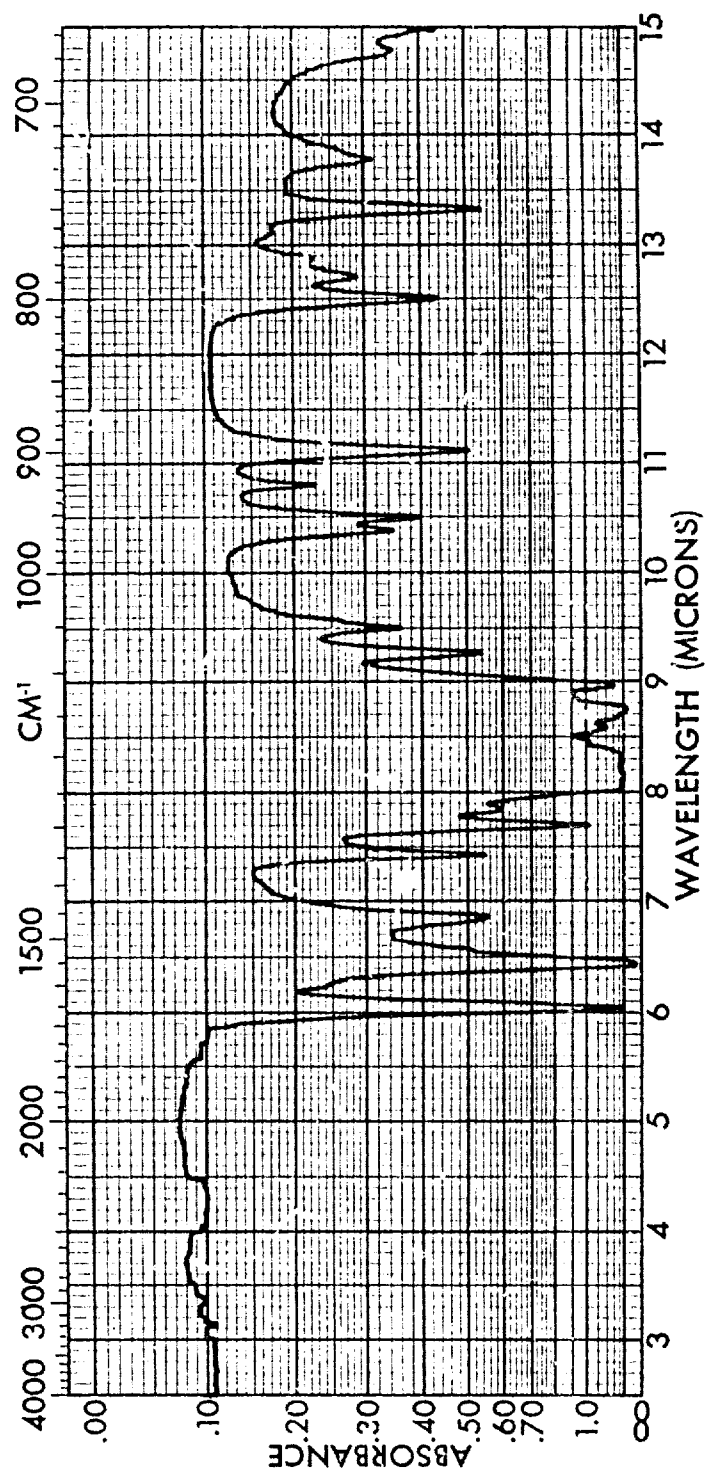


Fig. 42 - Infrared Spectrum of Thallium Decafluoro-2,4-heptanedionate
(Solid, Split Mull)

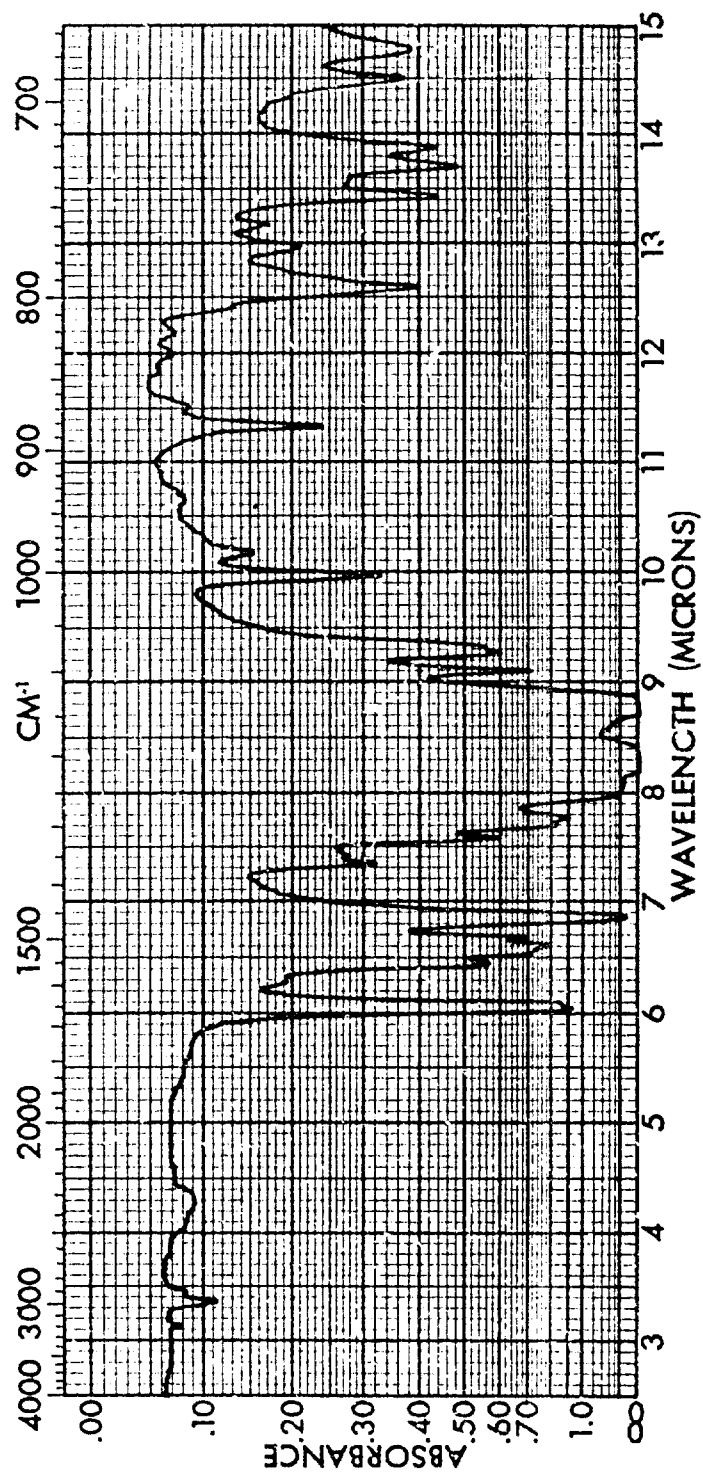


Fig. 43 - Infrared Spectrum of Thallium
Octadecafluoro-2,4-undecanedionate
(Solid, Split Mull)

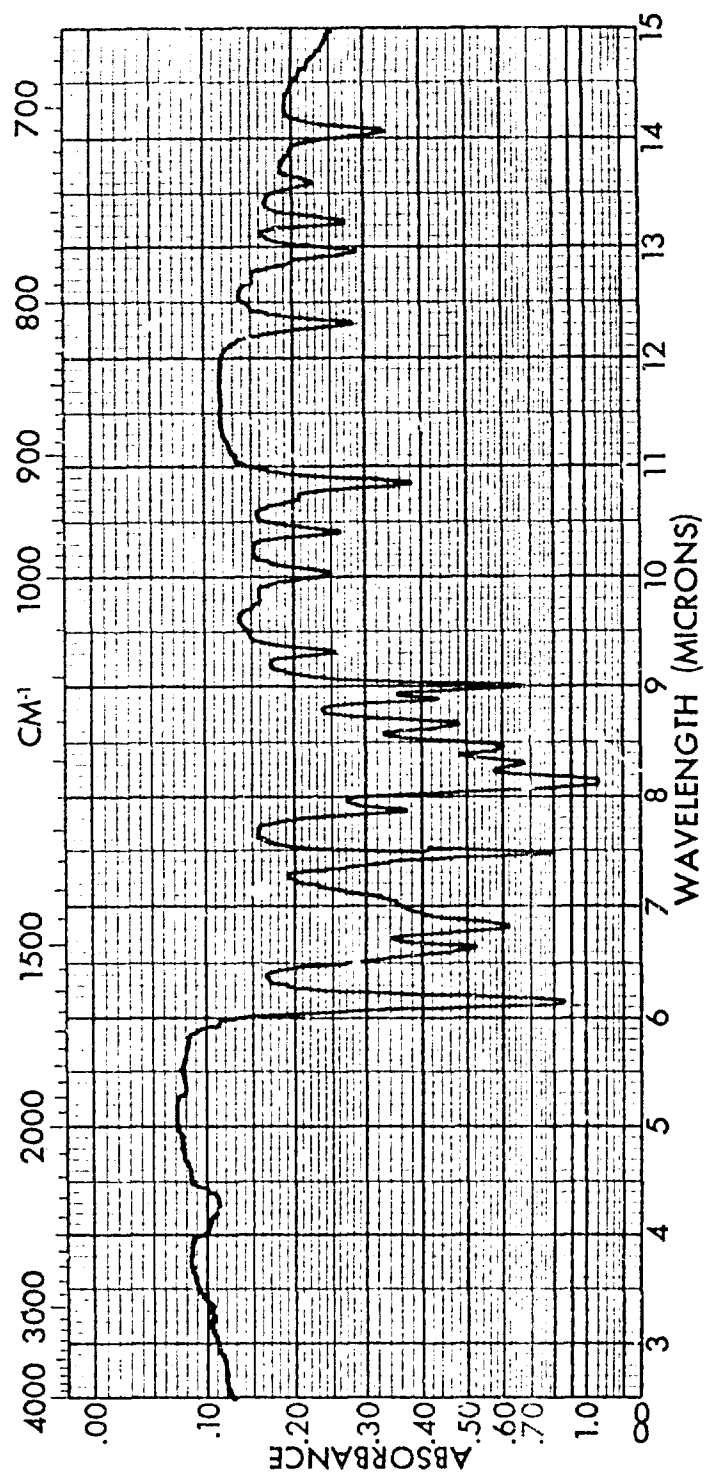


Fig. 44 - Infrared Spectrum of Thallium
Heptafluoro-2,4-heptanedionate
(Solid, Split Mull)

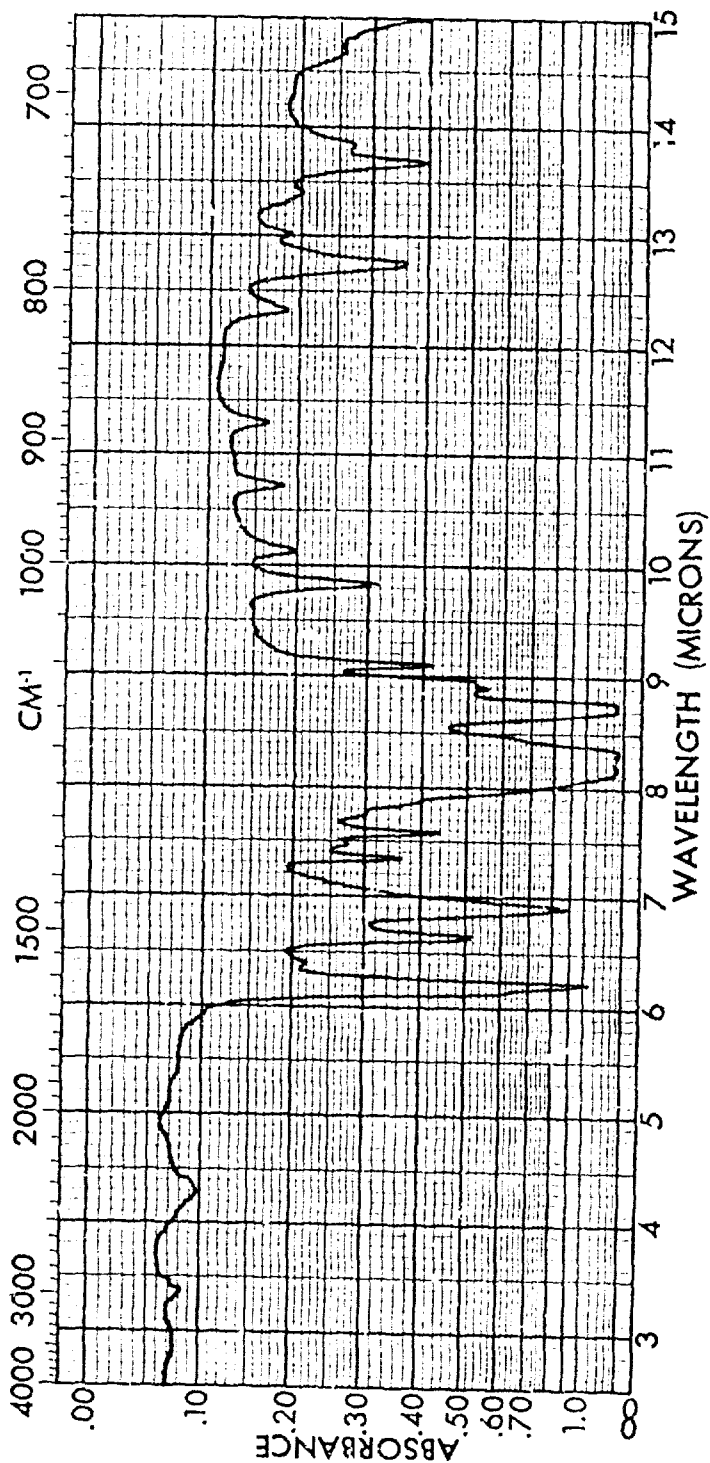


Fig. 45 - Infrared Spectrum of Thallium
Pentadecafluoro-2,4-indecanedionate
(Solid, Split Mull)